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Measurements of Low Vapor Pressures of Alkali Halides

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The vapor pressures over the crystalline salts have been measured in the neighborhood of 900°K by Knudsen's method for the chlorides and bromides of sodium, potassium and rubidium. Heats of vaporization have been calculated from the data.

INTRODUCTION

KNUDSEN'S method of molecular effusion[1] is very suitable for the measurement of low vapor pressures at high temperatures. In the experiments to be described this method is applied to determine the small vapor pressures of alkali salts below their melting points. The salt vapors passing through a small opening of known area in a definite time interval, at constant temperature, are condensed on a cold surface and their amount measured. The vapor pressure, P, is calculated from the formula

$$P=(m/a\cdot t)(2\pi RT/M)^{\frac{1}{2}},$$

where a is the area of the opening, t the time, T the temperature, R the gas constant, M the molecular weight and m the amount of condensed salt. The area of the hole is supposed to be negligible when compared with the area of the walls of the vessel and with the exposed surface area of the salt crystals. Similarly, the diameter of the opening must be small compared to the mean free path of the gas molecules.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus is shown in Fig. 1. The cylindrical iron oven O containing the salt crystals had an outside diameter of 5 cm and was drilled out on the inside to 2 cm. The six heating elements of "Globar" (carborundum composition) were led through six holes in the oven wall parallel to the axis of the oven and fastened to an iron ring G above the oven. The Globar rods were mounted in parallel and connected, at their lower ends, by small clamps and a copper wire. Small porcelain rings insulated the Globar elements from the oven wall. When heated to 650°C, the oven had a resistance of about 4Ω and carried 5 amperes. In order to facilitate a good contact and a uniform heating both ends of the six rods had been dipped, when manufactured, into a metal solution. Untreated rods proved to be unsatisfactory.

The oven was open at its lower end. Correspondingly, the plate P carrying the salt crystals could be lifted and fit tightly into the interior of the oven. After thorough drying, the salt was sealed, under vacuum, into small bulbs L made of thinly blown Pyrex glass, and mounted somewhat higher than the lowered position of P. The bulb could be crushed by raising the plate against it with the help of a stopcock pulley and an attached string. When the salt was deposited on the plate, an electromagnet operating from the outside turned the empty bulb away and the plate was ready to be lifted into the oven.

[1] Knudsen, Ann. d. Physik **47**, 697 (1915).

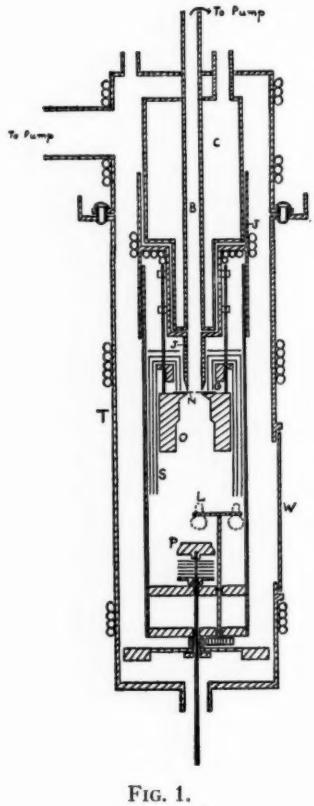

FIG. 1.

The nickel plate N screwed on top of the oven had in the center a small opening. Care was taken to have the opening drilled with a smooth and very thin edge. The salt vapors passing through the opening were condensed at the bottom of a copper stick (of about 20 cm in length) which could be lowered through the brass tube B into a position closely above the opening. The point of a steel needle welded to the end of the copper stick kept the proper distance of less than a millimeter from the nickel plate.

Particular precaution was necessary in order to keep the copper stick cold when the oven was heated. The brass tube B was led through a liquid-air container C carrying on its lower end (directly above the oven) a water-cooled brass jacket J. Little knobs with screws were soldered on J, holding the suspended oven on thin rods. The jacket was built in such a way as to form a prolongation of B and to reach almost as far as the nickel plate. It was important to have the copper stick fit as tightly as possible into the tube B and at the same time not to prevent a smooth sliding. Three chromium plated iron shields S surrounding the sides and the top of the oven reduced the heat loss. In this manner the copper stick was kept cold in a very satisfactory manner. The rod carrying the plate P had also several radiation shields attached. Both the liquid-air container and the oven were enclosed in a wide brass tube T which led to a steel mercury diffusion pump. This brass tube as well as the Pyrex plate glass window W which was sealed into T with De Khotinsky cement were water-cooled. The detachable lower part of T was screwed on to the upper part, the joint being sealed with "Apiezon" sealing compound which has the advantage of requiring no heat to make the seal.

The oven temperature was measured with two C.P. platinum-platinum 10 percent rhodium thermocouples which were calibrated against the freezing points of several metals. A hole was drilled into the oven wall to receive one thermocouple, the other being attached to the removable plate P. In order to attain good contact the thermocouple junctions were welded into two small iron plugs, tightly fastened into their respective holes with a screw. The cold junctions were kept at 0°C. The two thermocouples agreed within one degree.

In order to keep the temperature constant for a longer period of time, it was necessary to construct a voltage regulator. The voltage across the oven was balanced against two storage batteries which operated a relay. The relay controlled the height of a column of mercury surrounding a Globar stick thus controlling the resistance in series with the oven. This arrangement kept the oven temperature constant within 1°C during the measurements.

A measurement was carried out the following way: When a good vacuum and the desired temperature had been attained, P was loaded with salt and raised into the oven. Constant temperature being reestablished the copper stick was lowered by means of an attached string and stopcock. The moment when the stick had the proper position above the orifice was read from a stopwatch by observing the moment when a knot in the string had reached a mark on the glass tubing. After a measured length of time

the copper stick with the salt condensed on it was raised. Passing through a wide stopcock the stick could be removed without breaking the vacuum in the part containing the oven.

The condensed salt was washed from the copper stick and the solution carefully condensed by evaporation so that, by titrating it with 1/50-normal silver nitrate solution, the change in color could be easily distinguished. A drop of a 10 percent solution of potassium chromate was used as indicator. A burette of 5 cc with gradings of 0.01 cc permitted titration of small amounts of salt solution. One cc could be titrated to within 1 percent.

The area of the opening was measured with a comparator, the measurement of the diameter being accurate to 0.3 percent. Two different sizes of holes (0.01574 cm², 0.02122 cm²) were used for the measurements. The results agreed within the limit of experimental errors.

A correction was made to take into account the extension of the opening caused by heating the oven and with it the nickel plate. The correction amounts to an increase of the area of about 1.7 percent in the range of the temperatures used.

Experimental Results

Measurements were made on six salts, NaCl, NaBr, KCl, KBr, RbCl and RbBr. The vapor pressures at various absolute temperatures are recorded in Table I, and $\log_{10} P_{mm}$ is plotted against $1/T$ in Fig. 2. The solid lines of the figure represent the calculated vapor pressures from Eq. (3) with the values of the constants tabulated in Table IV.

Calculation of the Heat of Vaporization

There are three, essentially independent methods available for the calculation of the heat of sublimation, ΔH (vap.) from these and other known data.

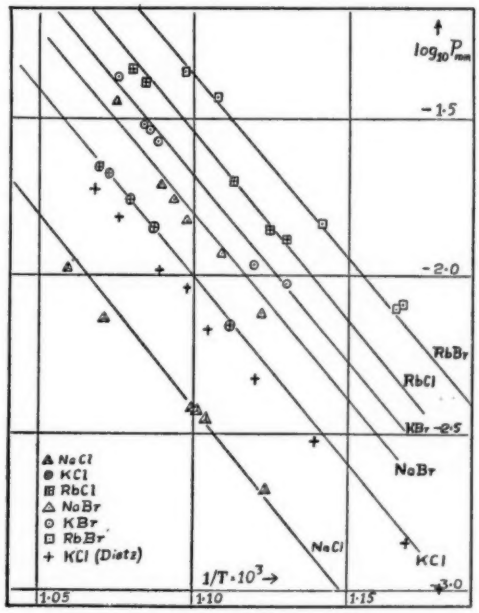

Fig. 2.

The first method is that of plotting logarithm of pressure against reciprocal of temperature and using the well-known formula

$$d \ln P/d(1/T) = -\Delta H/R. \qquad (1)$$

Owing to the rather small temperature and $\ln P$ interval for which these measurements are made the accuracy of this method is not very great. Small errors in the individual measurements result in rather large errors of slope. The results of this method, with the probable error, are recorded in column 2, Table II.

The second method involves the use of the measurements recorded in this article in conjunction with vapor pressure observations made by other workers over the liquid salt at much

Table I.

NaCl		NaBr		KCl		KBr		RbCl		RbBr	
T°K	$P_{mm}\times10^3$	T°K	$P_{mm}\times10^3$	T°K	$P_{mm}\times10^3$	T°K	$P_{mm}\times10^3$	T°K	$P_{mm}\times10^3$	T°K	$P_{mm}\times10^3$
890.2	2.11	891.2	7.65	899.4	6.98	884.9	9.48	885.0	13.1	856.4	7.99
905.7	3.55	901.5	11.8	920.1	14.3	893.1	10.8	889.4	14.1	857.7	7.90
907.9	3.74	910.8	15.1	926.5	17.8	918.9	26.8	898.5	19.9	876.2	14.5
909.5	3.82	914.1	17.5	932.3	21.2	921.1	29.1	922.2	40.8	902.7	36.8
933.6	7.32	917.4	19.5	935.3	22.0	922.5	30.2	925.6	45.0	911.4	44.4
944.1	10.5	930.1	35.6			929.4	43.0				

TABLE II.

SALT	ΔH(VAP.), 900°K, IN KCAL. FROM SLOPE OF THESE MEASUREMENTS	FROM P(VAP.) OVER LIQUID	FROM THEOR. ΔS CALCULATION	WEIGHTED AVERAGE	ΔH(VAP. 0°K) $=\Delta E$(VAP. 0°K) KCAL.
NaCl	50.5±2.5	53.6±1.5	52.4±1.7	52.4±1.7	55.2±2.0
NaBr	52.4±3.0	49.6±2.0	49.0±1.7	50.0±1.7	53.4±2.0
KCl	53.2±2.0	49.8±1.5	49.8±1.2	50.6±1.2	53.8±1.5
KBr	54.4±3.0	48.3±2.0	47.7±1.4	49.6±1.4	53.3±1.7
RbCl	49.3±2.0	46.6±2.0	48.7±1.7	48.1±1.7	51.3±2.0
RbBr	48.3±2.0	46.7±2.0	47.2±2.0	47.4±2.0	51.2±2.3

higher pressures and temperatures. Essentially this method resolves itself into finding two consistent equations for the vapor pressure of one salt, over the liquid and crystal, respectively. The equations must agree with the experimental observations over the liquid, and those of this work, respectively. They must also lead to the same vapor pressure at the melting point, T_f. They must further lead to a reasonable value for the heat of fusion ΔH_f.

Measurements of the vapor pressure over the liquid salt for NaCl, NaBr, KCl and KBr have been made by Wartenberg and Albrecht,[2] and on RbCl and RbBr by Wartenberg and Schulz.[3] All six salts have been measured Ruff and Mugdan.[4] These measurements all cover about the same range from some 50 to 760 mm, or from 1320°K to 1720°K. The temperature scale of Wartenberg and co-workers was slightly in error, and this correction has been applied in our calculations. The values of these workers all agree moderately well. Fiock and Rodebush[5] have measured NaCl, KCl and KBr from 5 to 50 mm (1180°K to 1430°K). Their measurements agree well with those of the previous workers. Horiba and Baba[6] have reported measurements on NaCl and KCl which appear to be in error at low pressures, but which agree moderately well at higher pressures with the other workers. Finally Maier[7] has recorded measurements on NaCl which are not in agreement with those of the others.

By plotting all these recorded results on a moderately large scale one is able to draw fairly reliable vapor pressure curves for NaCl, KCl and KBr from about 1200°K to 1700°K, and for NaBr, RbCl and RbBr from 1350° to 1700°K. In order to correlate these values with ours over the crystalline salt at about 900°K it is necessary to make some assumption concerning the change of heat of vaporization, ΔH_v, with temperature, part of which is due to the heat of fusion, ΔH_f, and part of which is due to the difference in specific heats of the liquid, respectively crystal, and the gas, ΔC_p.

We have used values for the heat of fusion taken from *International Critical Tables* for NaCl, KCl and RbCl, and have guessed at values for the other three salts. These values are recorded in column 2, Table III. Of these, only that for NaCl is really reliable. The heat of fusion of KCl is given to within 0.9 kcal. by I.C.T. That of RbCl appears to be inordinately low, and the results of our calculations indicate this. Nevertheless the error in these values will scarcely exceed 1.5 kcal.

The further assumption is then made that the specific heat of the condensed phase, crystal or liquid, is uniformly higher than that of the gas by $3R$. The exact value $3R$ is not of great importance, but since the temperature range over which the measurements stretch is some 800° the total correction is not of negligible importance.

With these assumptions of the value of the heat of fusion and the difference in specific heats of gas and condensed phase, it is only necessary to use one value of the vapor pressure over the liquid at high temperatures and one average of our values to calculate ΔH_v. Due to the enormous pressure range considered, a range of about one hundred thousand-fold, comparatively little error is introduced by uncertainties in the vapor pressures themselves. The greatest single error is one of about 0.75 kcal. to 0.85 kcal. due to the uncertainty in the heat of fusion. The final results with the probable errors are tabulated in column 3, Table II.

The third method by which ΔH(vap.) may be calculated is to evaluate the entropy change in

[2] Wartenberg and Albrecht, Zeits. f. Electrochem. **27**, 162 (1921).
[3] Wartenberg and Schulz, Zeits. f. Electrochem. **27**, 568 (1921).
[4] Ruff and Mugdan, Zeits. f. anorg. allgem. Chemie **117**, 161 (1921).
[5] Fiock and Rodebush, J. Am. Chem. Soc. **48**, 2522 (1926).
[6] Horiba and Baba, Bull. Chem. Soc., Japan **3**, 11 (1928).
[7] Maier, Techn. Papers, Bureau of Mines, Washington (1925).

sublimation theoretically, and to use one measurement of pressure to determine ΔF. Using

$$-\Delta F_v = RT \ln P = -\Delta H_v + T\Delta S_v \qquad (2)$$

ΔH_v can be immediately calculated.

The entropies of crystalline NaCl, KCl, NaBr and KBr are known at room temperature, the latter somewhat unsatisfactorily. The specific heat of KCl has been measured up to 600°K, and the curve is easily extrapolated to higher temperatures since it differs but little from the value $6R$. Using similar extrapolations for NaCl, NaBr and KBr give "experimental" entropies for these four crystalline salts at 900°K. Since the greater part of the entropy is present at room temperature this method appears to be fairly satisfactory.

The measurements of Barnes[8] on the frequencies of the alkali halide crystals enable us to calculate the entropies of the salts by assuming six Debye degrees of freedom with the measured frequencies. The agreement in the case of NaCl, NaBr, KCl and KBr with the values obtained from specific heats gives us some confidence in the use of these values for the other two salts.

Sommermeyer[9] has measured the fundamental frequencies of several of the gaseous alkali halides, among them KBr and RbCl. The frequencies of the other molecules may be extrapolated without great error. Maxwell, Hendricks and Moseley[10] have determined the interatomic distances in the molecules by electron diffraction. These data enable the calculation of the entropy of the gas to be made. A small correction for anharmonicity and rotational stretching has been introduced.

The data and results of the calculations of entropy are given in Table III. From these values of ΔS(vap.) and the values of $\ln P$ at 900°K the values of ΔH_v at 900°K have been calculated and are recorded in column 4, Table II.

The weighted average values of ΔH(vap. 900°K) are in column 5, and ΔH(vap. 0°K) in column 6 of Table II.

The Vapor Pressure Curve

Finally, having arrived at a most probable value for ΔH(vap. 900°K) we may return to the second method used to determine ΔH, and, reversing the method calculate an equation for $\log_{10} P$. We use the form

$$\log_{10} P_{mm} = -A/T - 3\log_{10}(T/1000) + C, \qquad (3)$$

in which the unaccustomed $\log T$ term enters from the assumed $\Delta C_p = -3R$ previously discussed. At any temperature

$$\Delta H(\text{vap. } T) = 4.5738A - 3RT. \qquad (4)$$

The constants A and C for liquid and crystal are tabulated in Table IV. We should have $4.57(A_{\text{cryst}} - A_{\text{liq}}) = \Delta H_f$, but since the integrated error in the assumption that C_p (gas) $- C_p$ (condensed) $= -3R$ is empirically taken into this term we cannot attach any significance to its value.

The constants tabulated fit P, to within the experimental error, with the best average of the results of the various workers mentioned previously. Presumably they can be counted on to

[8] R. B. Barnes, Zeits. f. Physik **75**, 723 (1932).
[9] K. Sommermeyer, Zeits. f. Physik **56**, 548 (1929).
[10] L. R. Maxwell, S. B. Hendricks and V. M. Moseley, Phys. Rev. **52**, 968 (1937).

Table III.

Salt	ΔH_f kcal.	Crystal: Frequencies (Barnes)[7] T	Crystal: S (900°K) cal./deg. From ν	From C_p	Probable Value	Gas: Frequencies (Sommermeyer)[9] cm^{-1}	Interatomic Distances (Hendrick)[9] 10^{-8} cm	S 900°K cal./deg.	ΔS 900°K cal./deg.	$T\Delta S$ kcal. 900°K
NaCl	7.22	234.2	32.0	31.5	31.5±0.9	374	2.51	64.9±0.7	33.4	30.1±1.5
NaBr	(6.9)	191.7	34.3	35.1	35.1±1.1	330	2.64	67.5±0.5	32.4	29.2±1.5
KCl	5.52	202.4	33.7	34.3	34.3±0.6	348	2.79	66.7±0.5	32.4	29.2±1.0
KBr	(5.3)	162.6	36.3	37.8	37.8±1.0	283	2.94	69.4±0.3	31.6	28.4±1.2
RbCl	4.59	168.8	35.8		36.3±1.4	253	2.89	69.5±0.3	33.2	29.9±1.5
RbBr	(5.1)	125.6	39.4		39.9±1.4	198	3.06	72.2±0.5	32.3	29.1±1.8

TABLE IV. *For use in* $\log_{10} P_{mm} = -A/T - 3\log_{10}(T/1000) + C$.

SALT	NaCl	NaBr	KCl	KBr	RbCl	RbBr
A(cryst.)	12629	12104	12229	12001	11674	11514
C(cryst.)	11.345	11.391	11.341	11.391	11.157	11.156
A(liq.)	11477	10480	10710	10490	10307	10224
C(liq.)	10.275	9.811	9.909	9.883	9.772	9.805
M.P.°K	1077	1028	1045	1003	988	955

duplicate the true vapor pressures to within twenty or thirty percent over the whole temperature range from about 850°K to 1700°K.

The curves of Fig. 2 are those corresponding to the calculated constants of Table IV in the neighborhood of our measurements. The results of Dietz[11] have been plotted in Fig. 2 but neglected in making the calculations.

Dietz's measurements are uniformly about thirteen percent lower than ours which may be regarded as not unsatisfactory agreement. The difference in ΔF calculated from his measurements and ours is 0.5 kcal., and both methods of calculation if applied to his measurements instead of ours would result in a value of ΔH approximately 0.5 kcal. higher than that given here.

[11] Dietz, J. Chem. Phys. **4**, 575–580 (1936).

TABLE V. *Energies in kilocalories of reactions at 0°K.*

SALT	NaCl	NaBr	KCl	KBr	RbCl	RbBr
$MX_{cryst} \rightarrow MX_{gas}$	55.2	53.4	53.8	53.3	51.3	51.2
$MX_{cryst} \rightarrow M^+_{gas} + X^-_{gas}$	183.1	174.6	165.4	159.3	160.7	153.5
$MX_{gas} \rightarrow M^+_{gas} + X^-_{gas}$	127.9	121.2	111.6	106.0	109.4	102.3
$MX_{cryst} \rightarrow M_{gas} + X_{gas}$	152.6	139.1	152.6	140.5	152.8	141.6
$MX_{gas} \rightarrow M_{gas} + X_{gas}$	97.4	85.7	98.8	87.2	101.5	90.4

THE HEATS OF OTHER REACTIONS

The lattice energies of these salts give the energies of dissociation at absolute zero of the crystalline salt into gaseous ions. These have been calculated by Mayer and Helmholz.[12] The difference between lattice energy and heat of sublimation at absolute zero gives the heat (or energy) of dissociation of the gaseous molecule at 0°K. Similarly from the data tabulated by Bichowsky and Rossini[13] the energy differences (at 0°K) of crystalline salt and its component gaseous atoms can be calculated. The difference of these values and the heats of sublimation give the energy of dissociation of the gaseous molecule into atoms. The energies of these reactions at 0°K are tabulated in Table V.

[12] Mayer and Helmholz, Zeits. f. Physik **75**, 19 (1932).

[13] Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold, 1936).

The Mechanism of Formation of Mercury Hydride and Mercury Deuteride. Optical Excitation of Cadmium Deuteride

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(Received March 3, 1938)

An attempt has been made to secure resonance excitation of HgH by illuminating (1) a mixture of mercury, hydrogen and nitrogen, and (2) a mixture of mercury and water vapor, with the light from a mercury and hydrogen discharge. This discharge emitted a fairly intense HgH spectrum. Weak HgH band radiation was observed which was similar to that secured when the same mixtures were illuminated with a discharge tube which did not emit the HgH radiation. Inability to secure resonance is evidence that the weak band radiation is due to HgH molecules formed in excited states which dissociate after emission. Experimental evidence is presented which indicates that the formation process is

$$Hg6^3P_1+H\rightarrow HgH^2\pi_{1/2,\ 3/2}+\Delta,$$

where Δ is an energy parameter. Essentially similar results were secured for HgD. Resonance excitation of CdD was observed when a mixture of cadmium and deuterium was illuminated with a cadmium and deuterium discharge.

INTRODUCTION

GAVIOLA and Wood[1] secured the HgH band radiation from a mixture of mercury, hydrogen and nitrogen illuminated with a mercury vapor lamp. They presented indirect evidence indicating that the molecule is formed in an excited state and dissociates after emission. They also observed the molecular radiation when mercury and water vapor was illuminated with a mercury vapor lamp.

Similar experiments were performed by Beutler and Rabinowitch[2] and F. F. Rieke.[3] They assumed that the molecule is formed in the normal state and subsequently excited by a collision with an excited mercury atom. This was postulated because of the abnormal rotation of the HgH molecule excited in this manner.

It should be possible to determine which is the process occurring by comparing the band radiation secured when a source emitting the HgH radiation is used with that secured when a mercury discharge free of hydrogen is used.

If the HgH molecules were present in the normal state they would absorb molecular radiation from the source and produce a fairly intense HgH spectrum. (This type process will be referred to as resonance excitation.) With the hydrogen-free source the only method of raising HgH molecules to excited states is by collisions of the second kind with excited mercury atoms. One would expect a much weaker band radiation to result from this process.[4]

On the other hand if the molecules do not exist in the normal state for an appreciable length of time because of their low energy of dissociation[5] (0.37 volts) resonance excitation and collision excitation would be impossible. Any band radiation observable should then be the same as excited by all sources emitting the atomic mercury spectrum with the same intensities. In addition, the band radiation would have to result from molecules formed in excited states which dissociate after emission.

APPARATUS

The apparatus was essentially the same as that described by Bender[4] and consisted of a quartz resonance tube encircled by a spiral section of the discharge tube. Spectrograms of the fluorescence were secured with two instruments, one having an average dispersion of

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† The main content of a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the department of physics, in the Graduate College of the State University of Iowa, August, 1937.

[1] E. Gaviola and R. W. Wood, Phil. Mag. **6**, 1191 (1928).

[2] H. Beutler and E. Rabinowitch, Zeits. f. physik. Chemie, **B8**, 231 (1930).

[3] F. F. Rieke, J. Chem. Phys. **4**, 513 (1936).

[4] P. Bender (Phys. Rev. **36**, 1535 (1930)) has observed that resonance excitation of CdH is more than fifty times as intense as the weak band radiation which can be secured when the cadmium and hydrogen mixture is illuminated with a cadmium discharge not emitting the CdH spectrum. As the energies involved in the possible excitation processes are of the same order of magnitude as those obtaining for mercury and hydrogen, one would expect similar results for the optical excitation of HgH.

[5] E. Hulthen, Zeits. f. Physik. **50**, 319 (1928).

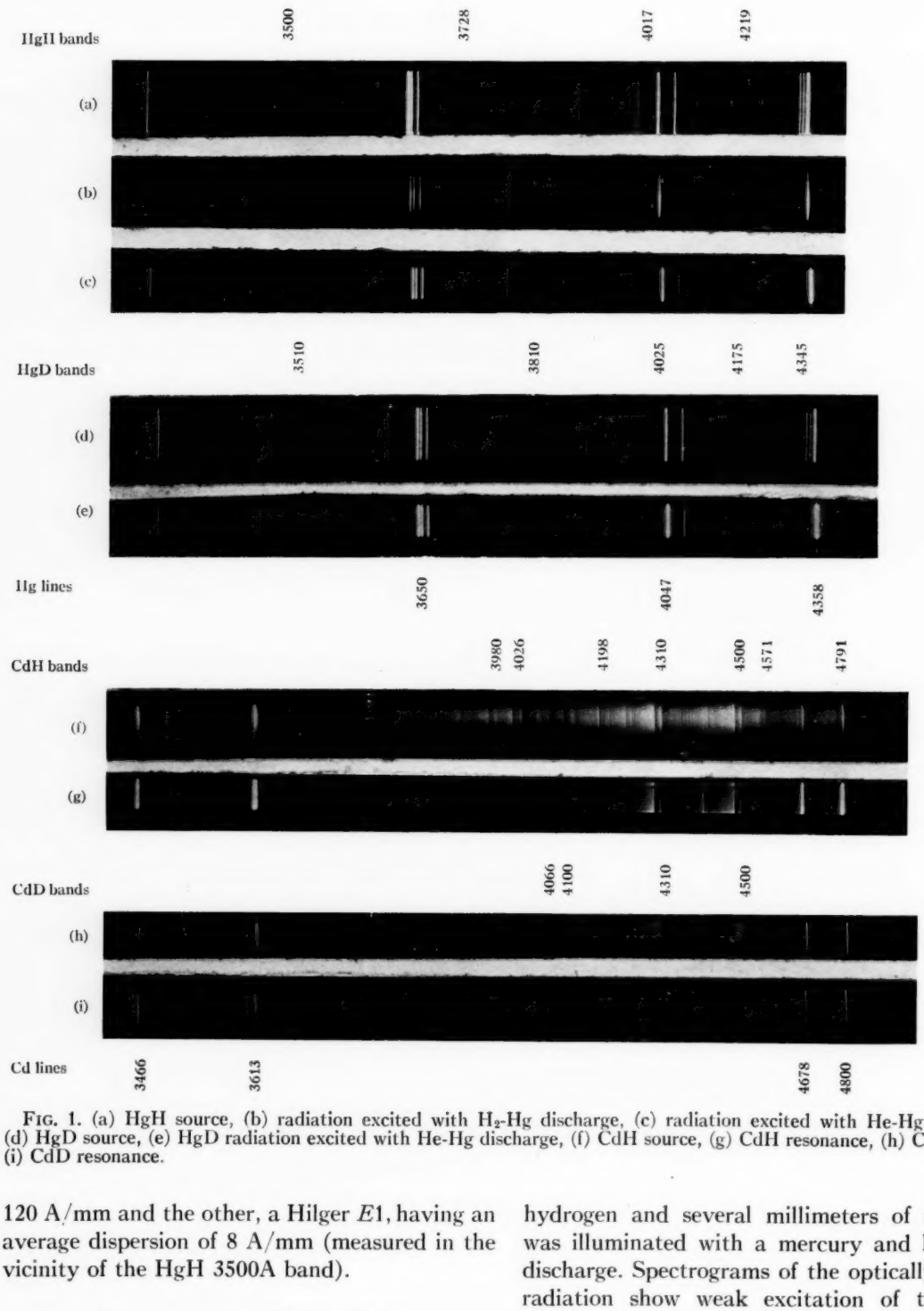

FIG. 1. (a) HgH source, (b) radiation excited with H_2-Hg discharge, (c) radiation excited with He-Hg discharge, (d) HgD source, (e) HgD radiation excited with He-Hg discharge, (f) CdH source, (g) CdH resonance, (h) CdD source, (i) CdD resonance.

120 A/mm and the other, a Hilger $E1$, having an average dispersion of 8 A/mm (measured in the vicinity of the HgH 3500A band).

RESULTS FOR HgH AND HgD

A mixture of mercury vapor (approximately 40°C), about one-hundredth of a millimeter of hydrogen and several millimeters of nitrogen[6] was illuminated with a mercury and hydrogen discharge. Spectrograms of the optically excited radiation show weak excitation of the HgH bands belonging to the $^2\Pi_{1/2,\,3/2} \rightarrow {}^2\Sigma_{1/2}$ system

[6] Nitrogen was produced by the decomposition of sodium azide in a vacuum. Hydrogen and deuterium were produced by electrolytic decomposition of water and deuterium oxide.

with a rotational structure differing from that of the source but similar to that observed by previous experimenters.[1-3] The same structure was also observed when the source was operated with helium in place of hydrogen. Frequent spectroscopic examinations of this source were made to be sure no hydrogen contamination was present. Excitation of the HgH band radiation was thus observed to be independent of the presence of HgH in the source.

The failure to secure resonance must mean that HgH is not present in the normal state. Hence, the HgH band radiation observed was produced by molecules formed in excited states. Fig. 1 (a), (b) and (c) shows spectrograms of the source and of the optically excited radiation.

Wood and Gaviola[1] assumed that the excited HgH molecules were formed from mercury atoms in 6^3P states and atomic hydrogen. The large energy discrepancies involved in such reactions are rather unsatisfactory and an attempt was made to establish definitely which excited states are responsible for the formation of the molecules.

A consideration of the energy levels of mercury shows that the $Hg7^3S_1$ state possesses the requisite amount of energy to form HgH $^2\Pi_{1/2,\ 3/2}$ by means of an energy exchange with a hydrogen molecule. Interactions of atomic or molecular hydrogen with mercury atoms in other states of rather high probability involve larger discrepancies than encountered for $Hg7^3S_1$ or $Hg6^3P$ and thus need not be considered.

As the $Hg7^3S_1$ state is populated principally by absorption of λ4047 by $Hg6^3P_0$ and λ4358 by $Hg6^3P_1$, the HgH band radiation should disappear when these wave-lengths are filtered out of the exciting radiation if the HgH molecules are formed by these atoms.[7] When the filtered source was used the *HgH fluorescence still occurred* and it must be concluded that mercury atoms in the $6^3P_{0,\ 1}$ states are responsible.[8]

The energy above that required for formation in a low rotational state must be divided between energy of rotation, and energy of translation of the molecule and a third body. Classical considerations of an approximate character show that almost all of this energy could appear as energy of rotation of the HgH molecule. This would account for the abnormal rotation which has been observed.

It will be observed that the process

$$Hg6^3P_{0,\ 1}+H\rightarrow HgH\ ^2\Pi_{1/2,\ 3/2}+\Delta$$

demands the presence of free atomic hydrogen whereas the process

$$Hg6^3P_0+H_2\rightarrow HgH\ ^2\Sigma_{1/2}+H+\Delta$$

suggested for formation in the normal state involves molecular hydrogen. The effect of oxygen on the optically excited radiation presents indirect evidence that it is necessary to have atomic hydrogen to secure the band radiation. Admission of a small amount of oxygen extinguishes the HgH radiation and causes the OH band in the vicinity of λ3070A to shine out immediately. Wood and Gaviola[1] performed this experiment but it has been repeated because of its significance. In addition it has been observed that the intensity of the OH band falls off rapidly after the admission of the oxygen. Wood and Gaviola[1] proposed the reaction

$$Hg'+O_2\rightarrow Hg+O_2',$$
$$O_2'+H\rightarrow O+OH,$$
$$H_2+O\rightarrow H_2O.$$

The extinction of the OH band would indicate that the reaction

$$H+OH\rightarrow H_2O$$

was also occurring. The water vapor formed was frozen out in the dry ice and acetone trap.

It would be of interest to know which Hg ^3P atoms were uniting with atomic hydrogen to form HgH $^2\Pi_{1/2}$ and HgH $^2\Pi_{3/2}$. From considerations of conservation of angular momentum about the axis of symmetry,[9] $Hg6^3P_0$ plus hydrogen can produce only HgH $^2\Pi_{1/2}$ whereas $Hg6^3P_1$ plus hydrogen can produce both HgH $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$.

Under the conditions of this experiment $Hg6^3P_0$ atoms were more abundant than $Hg6^3P_1$, yet the λ3500A ($^2\Pi_{3/2}\rightarrow{}^2\Sigma_{1/2}$, $0\rightarrow0$) band was more intense than λ4017A ($^2\Pi_{1/2}\rightarrow{}^2\Sigma_{1/2}$, $0\rightarrow0$). (Refer to Fig. 1.) It has also been found that the

[7] A bromine and chlorine cell absorbs effectively in this region.

[8] F. F. Rieke (reference 3) also secured the molecular radiation using a filtered source. His filter was used for a different purpose, however.

[9] R. S. Mulliken, Rev. Mod. Phys. **4**, 26 (1932).

intensity of these bands increases somewhat less than linearly with increasing nitrogen pressure in the range from zero to three millimeters pressure. This has been determined by visual examination of a series of exposures for which the time of exposure was halved when the nitrogen pressure was doubled. An approximately linear relationship should exist if mercury atoms in the 6^3P_1 state were the combining atoms. On the other hand, if $Hg6^3P_0$ were the reacting atoms the band intensity should be approximately a quadratic function of the nitrogen pressure. The first $Hg6^3P_0$ atom produced by a collision of $Hg6^3P_1$ with a nitrogen molecule would be used to dissociate a hydrogen molecule, a second nitrogen molecule would be used to form an $Hg6^3P_0$ which would combine with one of the free hydrogen atoms. Thus the relationship between nitrogen pressure and band intensity, and the intensity of λ4017A compared with λ3500A, both indicate that $Hg6^3P_1$ were the reacting atoms.

The energy relations obtaining for mercury and water vapor are more favorable for formation of HgH in the normal state.[2, 3] However, an attempt to secure resonance when mercury vapor in the presence of water vapor at a pressure of several millimeters of mercury was illuminated with a discharge emitting the HgH radiation gave negative results. Further, a weak HgH band radiation was observed which was similar to that secured when a mercury-helium discharge was used. It must therefore be concluded that the principal reactions which occurred were

$$Hg6^3P_0+H_2O\rightarrow Hg6^1S_0+H+OH+\Delta \quad \text{and}$$
$$Hg6^3P_1+H\rightarrow HgH\ ^2\Pi_{1/2,\ 3/2}+\Delta \quad \text{etc.}$$

That free atomic hydrogen is necessary for the formation of the molecules is further substantiated by comparing the HgH fluorescence secured when the water vapor in the resonance tube was circulated by pumping through a capillary tube during the exposure with that secured when the tube was shut off from the pumping system. The intensity of the fluorescence was much greater in the second case.

The rotational intensity distribution observed in this case was intermediate between that secured for the mercury, hydrogen and nitrogen combination and that observed for the source. (This is in agreement with the results of F. F. Rieke.[3]) Other conditions being unchanged increasing the water vapor pressure shifted the rotational intensity distribution in the bands toward that of the source.

Substitution of deuterium for hydrogen in the combination mercury, hydrogen and nitrogen, and excitation with a mercury-helium discharge free of hydrogen produced an HgD fluorescence similar in most respects to the HgH fluorescence already described. Fig. 1 (d), (e) shows spectrograms of the source and optically excited radiation. Comparing these spectrograms with those of Fig. 1 (a), (b), (c) it will be observed that the HgD band heads are somewhat more prominent than the corresponding heads for HgH. Also, for HgD, the $^2\Pi_{1/2}\rightarrow{}^2\Sigma_{1/2}(1\rightarrow0)$ band is more intense than $^2\Pi_{1/2}\rightarrow{}^2\Sigma_{1/2}(0\rightarrow0)$ which is not true for HgH. The spectrograms of the source and fluorescence both show a peculiar band structure in the region of λ3550A which has not been identified.

Resonance Excitation of Cadmium Deuteride

Bender[4] observed that the effectiveness of hydrogen in quenching the cadmium resonance radiation is due to the fact that an excited cadmium atom in collision with a hydrogen molecule produces CdH in the normal state. He was also able to secure resonance excitation of these molecules.

This experiment was repeated and extended to include the optical excitation of CdD. Fig. 1 (f, g, h and i) shows typical spectrograms of the CdH source, CdH resonance, CdD source and CdD resonance. Considerable difficulty was experienced in securing a pure CdD source. The source was first operated with helium and then with deuterium. After continued operation and frequent changes of the deuterium the source emitted a practically pure CdD spectrum.

In conclusion, the writer wishes to express his sincere appreciation to Professor A. Ellett for his excellent guidance and inspiration during the period of this investigation.

Infra-Red Absorption Bands in the Spectrum of Deutero-Formaldehyde

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(Received March 26, 1938)

The spectrum of deutero-formaldehyde in the infra-red has been studied from 2.0μ to 13.0μ and seven absorption bands have been found. With these data and the data on the spectrum of the ordinary formaldehyde available it has been possible, making use of the product relations of Redlich, to identify with considerable certainty the fundamental frequencies of the H_2CO and D_2CO molecules, respectively, as: $\nu_1=2780$ cm^{-1}, $\nu_2=1750$ cm^{-1}, $\nu_3=2875$ cm^{-1}, $\nu_4=1503$ cm^{-1}, $\nu_5=1278$ cm^{-1}, $\nu_6=1165$ cm^{-1}, and $\nu_1'=2056.4$ cm^{-1}, $\nu_2'=1700$ cm^{-1}, $\nu_3'=2160.3$ cm^{-1}, $\nu_4'=1106.4$ cm^{-1}, $\nu_5'=990.2$ cm^{-1} and $\nu_6'=938.0$ cm^{-1}. With this identification the valence force constants for the formaldehyde molecules have been computed.

I. INTRODUCTION

IN a recent publication[2] we have discussed the measurements made by us on two of the fundamental absorption bands in the spectrum of ordinary formaldehyde vapor. With these data one may make a reasonable assignment of the fundamental frequencies for that molecule, but since some controversy has existed concerning these we have considered it of sufficient importance to measure also the spectrum of the deuterium formaldehyde. If the six bands which we desire to assign as the fundamentals are correctly chosen we should expect to find in the spectrum of this isotopic molecule six corresponding bands; the frequencies of these latter six bearing definite and well-known relationships[3] to the frequencies of the former six. To establish the existence of these would serve as a convincing check on our identification and in this communication we wish to report on measurements which we have made on the absorption bands in the spectrum of D_2CO.

II. EXPERIMENTAL

A. Preparation of the D_2CO

The samples of D_2CO used in this investigation were made in the same manner as those used for measurements on the ultraviolet bands due to this molecule.[4] The method, which will be described in detail in that paper, consisted essentially of a photochemical union between deuterium and carbon monoxide under irradiation from a quartz mercury arc. The gaseous formaldehyde formed in this manner was liquefied and distilled three times to remove glyoxal. The colorless liquid remaining was allowed to polymerize slowly. This polymer was then introduced into our cells in weighed amounts whereafter the cells were evacuated and heated to a temperature sufficiently high to vaporize completely the sample.

Except for the preparation of the D_2CO the experimental procedure has here been almost identical to that in the measurements made and reported by us on two fundamental bands in the spectrum of the ordinary formaldehyde. The absorption cells were identical in length and construction to those used there and for the preliminary survey of the spectrum the same Wadsworth prism spectrometer was used. In this preliminary survey (Fig. 1) intense absorption was found near 4.3μ, 6.0μ, and in the region from 8.0μ to 13.0μ. For the high dispersion measurements on these regions the same prism-grating spectrometer referred to in our earlier work was utilized. Three different diffraction gratings were necessary; one ruled with 3600 lines per inch for the region near 4.3μ, a second ruled with 2000 lines per inch for the region near 6.0μ, and a third with 900 rulings to the inch for the region 8.0μ to 12.0μ. The slit widths used throughout these measurements included in each case approximately 1 cm^{-1} and deflections were taken with the cell in the beam and with the cell removed from the beam at equivalent intervals on the circle so that the data might be plotted as percent absorbed.

[1] Fellow of the Royal Society of Canada.
[2] E. S. Ebers and H. H. Nielsen, J. Chem. Phys. **5**, 822 (1937).
[3] O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935).
[4] To be published soon.

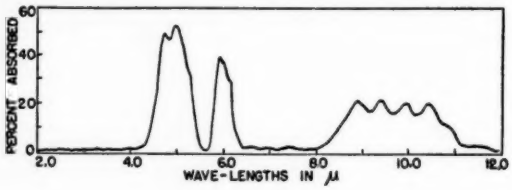

FIG. 1.

B. The 4.3μ region

This region corresponds to the region near 3000 cm^{-1} in the spectrum of H_2CO measured by one of us[5] and like that region it consists also of three badly overlapping bands which, however, have been sufficiently well resolved so that their characteristics may be identified. Two of them are of the type containing, P, Q and R branches while the third is of the type arising from oscillations of the electric moment perpendicular to the axis of symmetry. The centers of these have respectively been chosen to be 2056.4 cm^{-1}, 2209.0 cm^{-1} and 2160.3 cm^{-1}. The asymmetry of the molecule appears in this case to be great enough so that much of the sharpness of the rotation lines of the bands of the first type has been destroyed. An estimate of what here must be regarded as the spacing yields a value of about 1.85 cm^{-1}. In the second type of band, however, especially some distance from the center, one readily identifies a regularity of structure, the separations between the most prominent lines being about 7.6 cm^{-1}. In Fig. 2 is shown the absorption pattern characteristic of this region. The principal lines and their frequency positions are tabulated in Table I.

C. The 6.0μ region

This band is of the type with single P, Q and R branches and would seem to correspond to the region near 1750 cm^{-1} in the spectrum of ordinary formaldehyde. Unfortunately the band overlaps so badly with the intense water vapor fundamental of this region that it has been impossible to obtain any accurate data concerning the actual rotational structure of the branches. An envelope of this region obtained with widened spectrometer slits yields the curve shown in Fig. 3. The center appears to be very near to 1700 cm^{-1}.

D. The region 8.0μ to 12.0μ

This region has been sufficiently well resolved to show that it also is made up of three different bands that badly overlap each other. That of highest frequency is clearly of the type with single P, Q and R branches and must undoubtedly correspond to the similar band in H_2CO which lies near 1500 cm^{-1}. The remainder of this region must correspond to that in the spectrum of H_2CO reported by us in the work referred to in the introduction. It is clearly due to the oscillations of the electric moment normal to the axis of symmetry of the molecule and as in the case of H_2CO many of the spacings between the principal lines appear larger than the corresponding ones found in the band of similar character near 2160 cm^{-1}. These spacings are here equal approximately to 10 cm^{-1}, or about 25 percent larger than the former. In Fig. 4 is shown the absorption pattern of this region as determined by these measurements and in Table II will be found the frequency positions of many of the principal lines.

III. Discussion of the Experimental Results

With the completion of these measurements, fairly accurate information concerning the bands

[5] H. H. Nielsen, Phys. Rev. **46**, 117 (1934).

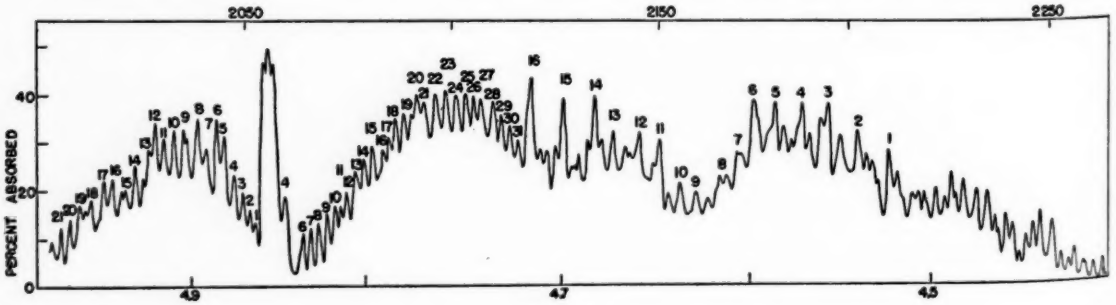

FIG. 2.

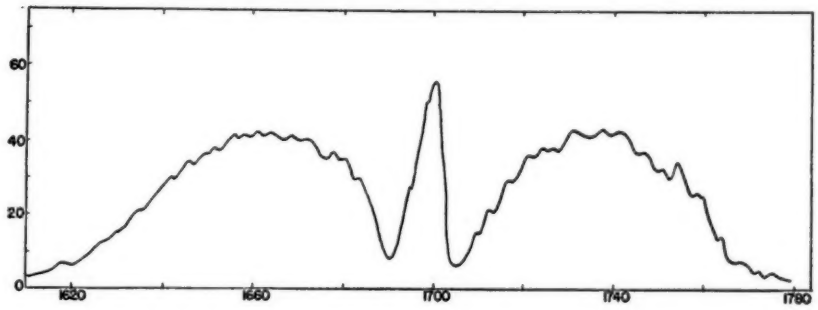

FIG. 3.

in the spectra of the formaldehyde is available and it seems possible now to make an assignment of the fundamental frequencies with a good deal of certainty. In making these assignments one may be guided by the fact that there are certain product relationships, which, as Redlich has shown, the frequencies belonging to any one symmetry class must fulfill. Our assignment of fundamental frequencies in the case of H_2CO and D_2CO is given in Table III using the notation of Dennison and Sutherland.[6] As we shall verify in the following paragraph, this assignment is consistent with the requirements derived by Redlich.

For H_2CO and D_2CO the normal oscillations divide up into three symmetry classes which include respectively, the frequencies ν_1, ν_2, ν_4; ν_3, ν_5; and ν_6. In terms of these the product relations of Redlich may be written in the following manner:

$$
\begin{aligned}
&(\nu_1\nu_2\nu_3/\nu_1'\nu_2'\nu_3')^2 \\
&\quad = (m_D^2 m_C m_O/m_H^2 m_C m_O)(M_{H_2CO}/M_{D_2CO}), \\
&(\nu_4\nu_5/\nu_4'\nu_5')^2 = (m_D^2 m_C m_O/m_H^2 m_C m_O) \\
&\qquad\qquad \times (A/A')(M_{H_2CO}/M_{D_2CO}), \\
&(\nu_6/\nu_6')^2 = (m_D^2 m_C m/m_H^2 m_C m_O) \\
&\qquad\qquad \times (B\cdot C/B'\cdot C')(M_{H_2CO}/M_{D_2CO}),
\end{aligned}
\tag{1}
$$

where ν_i and ν_i' are the frequencies of oscillation of the H_2CO and D_2CO molecules; A, B, C and A', B', C' their principal moments of inertia; m_H, m_C, m_O, etc., the masses of the component atoms and where M_{H_2CO} and M_{D_2CO} are the molecular masses of the two molecules. In order to make use of these relations to verify our assignment of frequencies it is necessary to know the values of A, B, C, A', B' and C'. The values A, B and C have been determined for H_2CO in the ground state, with considerable accuracy by Dieke and Kistiakowsky[7] who give the following values expressed in g cm^2: $A=24.33\times10^{-40}$, $B=21.39\times10^{-40}$, $C=2.941\times10^{-40}$. These same

TABLE I. *Frequency positions of lines in the 4.0μ region.*

−21	2011.2	1	2119.0	−3	2051.0	15	2081.7
−20	2014.0	2	2127.2	−2	2052.6	16	2083.3
−19	2015.3	3	2134.8	−1	2054.3	17	2085.5
−18	2017.7	4	2139.2	0	2056.4	18	2086.2
−17	2020.0	5	2149.6	1		19	2089.5
−16	2022.4	6	2151.3	2		20	2091.7
−15	2025.5	7	2157.0	3		21	2094.0
−14	2028.1	8	2160.3	4	2062.4	22	2096.8
−13	2030.2	9	2166.3	5	2064.0	23	2099.3
−12	2033.1	10	2170.9	6	2065.7	24	2101.6
−11	2035.0	11	2174.8	7	2067.3	25	2103.9
−10	2036.6	12	2180.6	8	2069.0	26	2106.4
−9	2038.2	13	2187.1	9	2070.6	27	2108.4
−8	2040.3	14	2193.9	10	2072.2	28	2110.7
−7	2043.8	15	2202.0	11	2073.9	29	2112.4
−6	2045.6	16	2210.8	12	2075.6	30	2114.2
−5	2047.8			13	2077.8	31	2115.9
−4	2049.4			14	2080.0		

TABLE II. *Frequency positions of lines in 11μ region.*

1	841.3 cm^{-1}	15	977.8 cm^{-1}
2	852.9	16	981.1
3	859.2	17	990.2
4	864.9	18	997.9
5	875.9	19	1002.1
6	887.8	20	1009.1
7	893.3	21	1014.4
8	906.4	22	1023.3
9	938.5	23	1033.3
10	949.1	24	1043.4
11	958.5	25	1053.8
12	962.4	26	1066.4
13	968.0	27	1103.8
14	974.5		

[6] G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. **148A**, 250 (1935).

[7] G. H. Dieke and G. B. Kistiakowsky, Phys. Rev. **45**, 4 (1934).

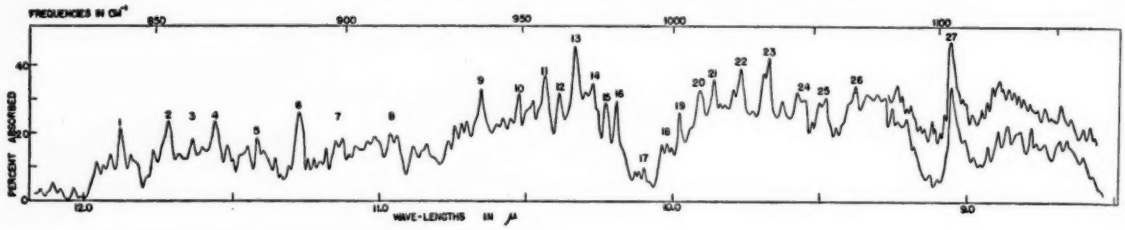

FIG. 4.

values are also found to be consistent with the infra-red absorption data. The bands in the spectrum of D_2CO, in particular those due to oscillations of the electric moment along the axis of symmetry, are hardly well enough resolved to make a complete rotational analysis feasible and hence, very accurate values for A', B', and C' cannot be determined from the data here presented. An estimate of the values of A', B', and C' can, however, be arrived at which is sufficiently accurate for use in Eqs. (1). We shall make use of the bands near 4.5μ which are probably as well resolved as any, to make these estimated values of A', B' and C'.

If we approximate the rotational motion of the D_2CO molecules by that of an equivalent symmetric rotator with the moments of inertia $\bar{A}$, $\bar{B}$ and $\bar{C}$ related to the actual moments of inertia A', B' and C' in the following manner $1/A=1/B=\frac{1}{2}(1/A'+1/B')$ and $\bar{C}=C'$ one obtains for the separations between principal lines in the bands arising from oscillations of the electric moment parallel and perpendicular to the axis of symmetry, respectively, the following values:

$$\Delta\nu_1=(h/4\pi^2)\tfrac{1}{2}(1/A'+1/B')$$

and $$\Delta\nu_2=(h/4\pi^2)[1/C'-\tfrac{1}{2}(1/A'+1/B')].$$

These assumptions are clearly less valid here than for H_2CO for here the asymmetry will be appreciably greater than for H_2CO, but still sufficiently good, when spacings not too near the center are considered to make the above test. For $\Delta\nu_1$ we have taken the value 1.85 cm^{-1} and for $\Delta\nu_2$ the value 7.6 cm^{-1} seems best. These values lead to $\bar{A}=\bar{B}=30.1\times10^{-40}$ g cm^2 and $\bar{C}=5.84\times10^{-40}$ g cm^2. Bearing in mind that $(1/\bar{A}+1/\bar{B})=(1/A'+1/B')$ and that $C'=A'-B'$ we obtain the values $A'=33.0\times10^{-40}$, $B'=27.2\times10^{-40}$ and $C'=5.84\times10^{-40}$ for the moments of inertia for the D_2CO molecule expressed in g cm^2.

For convenience we insert Table IV which sets forth the values of $\Pi(\nu_i/\nu_i')^2$ as computed from Redlich's Eqs. (1) as compared with the values determined from the experimental measurements. We feel the agreement is a satisfactory one when one considers that Redlich's derivation applies strictly speaking only when the oscillatory motion is harmonic, and offer it in support of our assignment of frequencies given in Table III. Certain writers have preferred the assignment $\nu_1(H_2CO)=2974$ cm^{-1} and $2\nu_4(H_2CO)=2780$ cm^{-1} to the one given by us. We cannot but feel that the frequency 2780 cm^{-1} is much too intense to be given the assignment $2\nu_4$ and that the much less intense band at 2974 cm^{-1} would fit much more consistently with this assignment. This opinion is supported also by the measurements made on the corresponding bands in the spectrum of the isotopic molecule. This question cannot definitely be settled, however, by resorting to Redlich's equation since either assignment gives agreement between experimental and computed values of $\Pi(\nu_i/\nu_i')^2$.

If the above assignment of frequencies be adopted as correct, we may make use of it to derive information concerning the forces binding the atoms of the molecule together. Certain assumptions are, in general, necessary concerning the nature of these forces and the one which here

TABLE III. *Assignment of frequencies in* H_2CO *and* D_2CO.

H_2CO	D_2CO
ν_1 2780 cm^{-1}	2056.4 cm^{-1}
ν_2 1750	1700.–
ν_3 2875	2160.3
ν_4 1503	1106.0
ν_5 1278	990.2
ν_6 1165	938.–
$2\nu_4$ 2974	2209.–

TABLE IV. *Values of* $\Pi(\nu_i/\nu_i')^2$.

Computed values	1.48	2.8	3.7
Experimental values	1.5	2.9	3.6

shall be made is that the actual interatomic forces may to a good approximation be replaced by valence forces. This assumption which has proved itself useful in a great many cases is a convenient one since the quantities which then may occur in the potential energy function are ones readily interpretable in chemical and physical theory. Using such forces, Lechner[8] has considered the oscillational motion of the XYZ_2 type of molecule in its own plane and has derived the following relations:

$$\nu_3^2\nu_5^2 = f_{13}\alpha' A,$$

$$\nu_3^2 + \nu_5^2 = f_{13}B + \alpha' C,$$

$$\nu_1^2\nu_2^2\nu_4^2 = f_{12}f_{13}\alpha D,$$

$$\nu_1^2 + \nu_2^2 + \nu_4^2 = f_{12}H + f_{13}I + \alpha K,$$

$$\nu_1^2\nu_2^2 + \nu_1^2\nu_4^2 + \nu_2^2\nu_4^2 = f_{12}f_{13}E + f_{12}\alpha F + f_{13}\alpha G,$$

where f_{12}, f_{13}, α and α' are to be regarded as force constants and A, B, C, D, E, F, G, H, I, and K are constants depending upon the masses of the atomic nuclei, the interatomic distances and the YZ_2 bond angle. f_{12} and f_{13} are, respectively, the force constants to be associated with displacements of the X, Y and Y, Z particles along the valence arm joining them together;

[8] F. Lechner, Wien Bericht. **141**, 633 (1932).

TABLE V.

Force Constants	Computed Frequencies		Measured Frequencies	
	H_2CO	D_2CO	H_2CO	D_2CO
$\alpha = 1.46 \pm .03$	$\nu_1 = 2780$	$\nu_1 = 2138$	$\nu_1 = 2780$	$\nu_1 = 2056$
$\alpha' = .57 \pm .01$	$\nu_2 = 1840$	$\nu_2 = 1625$	$\nu_2 = 1750$	$\nu_2 = 1700$
$f_{12} = 12.06 \pm .03$	$\nu_3 = 2825$	$\nu_3 = 2118$	$\nu_3 = 2875$	$\nu_3 = 2160$
$f_{13} = 4.22 \pm .14$	$\nu_4 = 1470$	$\nu_4 = 1115$	$\nu_4 = 1500$	$\nu_4 = 1106$
	$\nu_5 = 1267$	$\nu_5 = 997$	$\nu_5 = 1278$	$\nu_5 = 990$

α and α' the valence force constants associated with the deformation of the XZ_2 and the XYZ bond angles, respectively.

The interatomic distances may be computed from the values of the moments of inertia, the XZ_2 bond angle having been assumed to be tetrahedral or about 109°. The constants f_{12}, f_{13}, α and α' have then been evaluated from the above equations of Lechner using the fundamental bands observed for the H_2CO and the D_2CO molecules. The values obtained for these constants from the two isotopic molecules are in good agreement; in Table V the average value of these being set down together with the actually observed fundamental frequencies and a set of frequencies, computed by substitution of these average value force constants into the above equations of Lechner, for comparison.

The values seem to be in satisfactory agreement when one considers that the Lechner derivations are valid, in reality, only when the oscillational motion is harmonic.

The Change in Absorption of Water at 4.7μ Due to Solutions

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(Received April 13, 1938)

A study has been made of the absorption of aqueous solutions of some halogen salts in the region of 4.7μ. It has been found that KF shifts the bands to shorter wave-lengths, while KCl, KBr, and KI shift the band to longer wave-lengths. The effect is explained as due to changes in hindered rotation as produced by the binding forces between the ions and water molecules. The changes in position of the band vary with concentration. The kind of positive ion does not seem to change the effect when the same negative ion is in solution.

STUDIES have been made by several investigators[1] of the effect on the absorption of water when different ions are present. The results obtained may be classified as changes in intensity and position of the water bands due to the presence of ions, other bands are observed which are not characteristic of water or the ions, and bands due to the ions. Some of these investigations on solutions have been made in the near infra-red region. Thicker cells can be used and the intensity of the source is greater. It is more difficult to interpret the results, however, as most of the bands in the near infra-red region are really two or more overlapping combination bands of the fundamental. A change in frequency may be a change in the relative intensities of the component bands, on account of the two fundamental bands of water at 2.72μ and 2.91μ. There is the same difficulty in the study of the 3μ region.

A study of the absorption spectra of liquid water shows bands at about 4.72μ and 5.75μ. These bands are not found in water vapor and are likely due to a combination of the 6.18μ water band and two hindered rotation frequencies at 20μ and 55μ. These bands are readily observed in the water spectrum, as can be seen from the top curve of Fig. 1. Also they have been observed in Raman spectra at 500 cm^{-1} and 170 cm^{-1} by Hibben.[2] The band at 5.75μ under higher resolution shows two parts at 5.56μ and 5.83μ. The angle between the OH and H in water vapor molecule is about 104.5° and in liquid water 107°. The change in the angle is small and the differences in the frequencies observed for the water vapor and liquid water are small. For example, the transverse vibration for water vapor occurs at 6.26μ and 6.18μ for water.

Since the presence of ions will not change the angle of the water molecule very much, it is not likely that the internal frequencies of the water molecule will be considerably altered by their presence. It appears that the effect of ions can best be studied in relation to the hindered rotation type of frequency which occurs at 20μ. In fact the 4.72μ band, which is a combination band with the 6.18μ band, should show the effect of the presence of ions. A study has been made of the effects of certain halogen salts on the absorption of water in this region.

The absorption spectra have been measured by using an infra-red spectrometer with a fluorite prism. At 5μ the effective slit width was 300A. The cells were made by placing a drop of the solution upon a fluorite plate. Another plate was placed over the first one and the two sealed together with wax. The plates were separated by mica washers about 0.02 mm in thickness.

In Fig. 1 is shown the absorption of water and solutions of KF, KCl, KBr, and KI. The cell thicknesses are about the same and the transmission in the region of 4.7μ is about 30 percent. The transmission of the KF is somewhat less than the other solutions. The concentration is greater and the absorption band shows a definite shift to shorter wave-lengths. In fact the shift of the position of maximum absorption in the solution is the important part found in this study. It can be seen from the curves that the band at 4.72μ in water occurs at 4.58μ in 5*N* KF solution, 4.76μ in the 3*N* KCl, 4.80μ in 4*N* KBr, and 5.85μ in 4*N* KI.

The next question considered was the effect on

* Now at Tulane University.
[1] G. E. Grantham, Phys. Rev. **18**, 339 (1921).
[2] Hibben, J. Chem. Phys. **5**, 994 (1938).

the position of this band due to the positive ion. Lithium and sodium salts of the halogens gave about the same positions for the different salts as are shown in Fig. 1. Also solutions of NH_4F, NH_4Cl, and NH_4Br were studied, to see the effect of a complex ion on the position of maximum absorption in this region. The results were of the same type as found for the potassium salts. The fluoride band is shifted to shorter wave-lengths, while the chloride and bromide are shifted to longer wave-lengths than the band in water. It appears that the bands for the ammonium salts occur at slightly longer wave-lengths than in the potassium salts. It can be seen in Fig. 2, for example, that the NH_4F band is about 4.62μ compared to 4.58μ for KF. This difference is about equal to the slit width of the spectrometer and may be produced by experimental error.

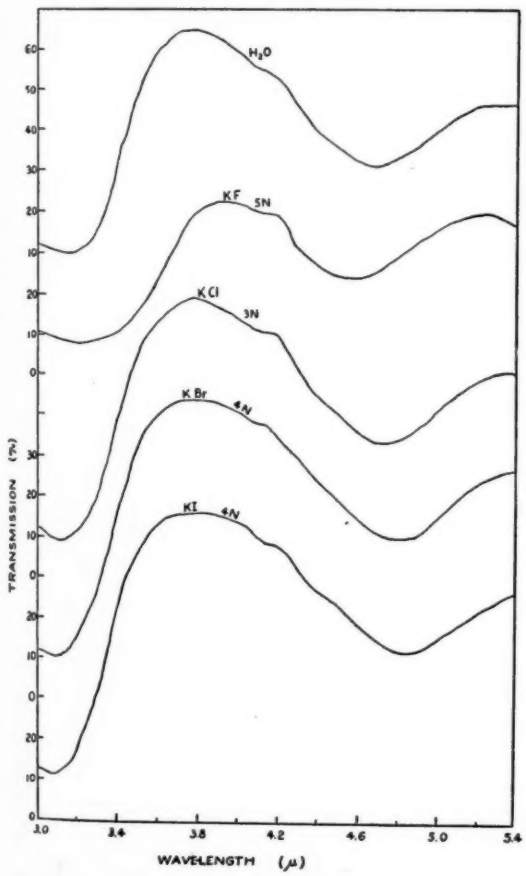

FIG. 1. A comparison of the absorption of water and aqueous solutions of KF, KCl, KBr, and KI in the region from 3.0μ to 5.4μ. The cell thickness is about 0.02 mm.

The next question considered in regard to the absorption of the solutions was the effect of the concentration on the position of the band. Concentrations from 0.75N to 6N of NaBr were measured in the region from 4.5μ to 6.5μ. The band gradually changed from 4.75μ to 4.88μ in the 6N solution. The solutions were also studied on a grating instrument of much higher resolution, but the bands were broad and of the same type as shown in Fig. 3. This shows that the band is not likely due to the overlapping of two bands which change the resultant maximum of absorption as the concentration is increased. The water band at 6.2μ does not change in position and this indicates that the changes observed in the 4.72μ band are due to the vibration of molecule with molecule or hindered rotation.

The structure of liquid water has been studied from various approaches, such as effect of pressure and x-rays. A theoretical study has been made by Bernal and Fowler.[3] They relate

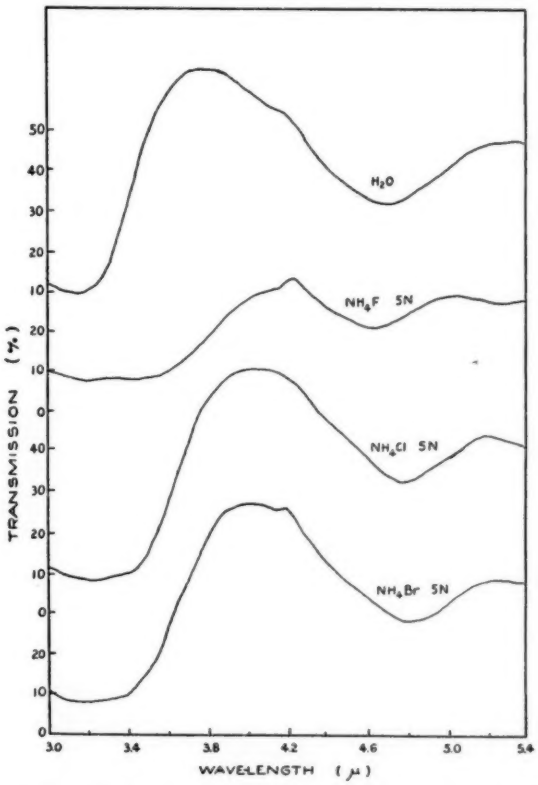

FIG. 2. The absorption of the ammonium salts in solution. The change in absorption at 3.3μ is produced by the NH_4 ion.

[3] Bernal and Fowler, J. Chem. Phys. 1, 515 (1933).

the structure, when ions are present, to a change in temperature. On the basis of their work, the fluorine ion would correspond to a lowering of temperature and the chlorine, bromine, and iodine to a rise in temperature; since it has been shown by Ganz[4] that the water band shifts to the longer wave-lengths when the temperature is increased.

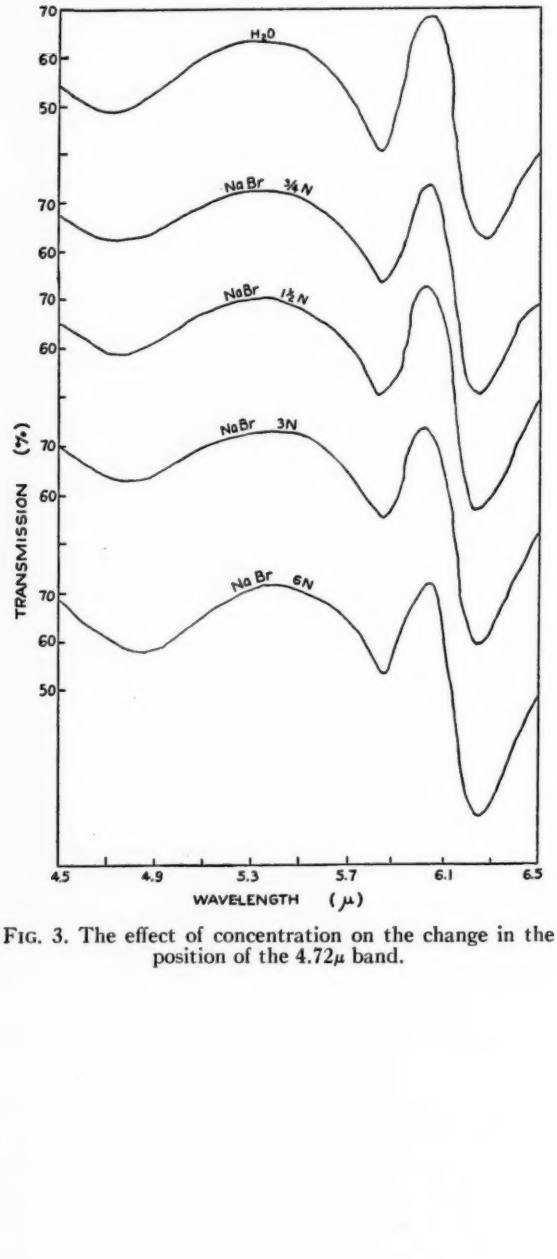

FIG. 3. The effect of concentration on the change in the position of the 4.72μ band.

The structure of water is produced by the linkage of hydrogen and oxygen of the neighboring molecules. For ice the structure is fixed and definite, but in water the linkage may not be so regular and may not extend in a regular way to include a large number of molecules in any group.

We may have a hindered rotation of the molecules in the group and that will give rise to three different frequencies, corresponding to the three principal moments of inertia of the molecule. Unless some force constants are assumed in relation to the forces between molecules, the positions of the three hindered rotations cannot be calculated. When a group of molecules is associated with an ion instead of a water molecule, the force constants will in general be different. When the binding force is increased, we would expect the hindered rotation frequency to be increased. The binding force of an ion will depend on its charge and the size of an ion. The size of the ion from fluorine to bromine is increasing and this is in agreement with the observation of the change in position of the band at 4.72μ. These results also show that the binding force of the fluorine ion is greater than that of water molecule to water molecule, and that the other halogen ions have a binding force less than water for water.

[4] Ganz, Ann. d. Physik **26**, 331 (1936).

Raman Spectra of Deutero-Ethylenes

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(Received February 12, 1938)

All the different ethylenes, have been prepared, their Raman spectra in the liquid state measured and classified. A comparison between experimental data and theoretical predictions permits an estimate of the order of magnitude of the anharmonicity.

(1) INTRODUCTION

MANY authors have attempted to calculate accurately the potential function of polyatomic molecules in their normal state. Although, such calculations have been made successfully for diatomic molecules, the study of visible and ultraviolet absorption spectra has given little information concerning polyatomic molecules. Only infra-red and Raman spectra furnish the experimental data necessary for a determination of this function. Unfortunately, the amount of such data is small, and it is not possible to calculate all the constants involved and *a fortiori* to check the proposed function. For instance, in the case of ethylene, investigated by several authors,[1] the harmonic potential function with regard to the planar vibrations (involving all the coupling terms), contains fifteen parameters, and infra-red and Raman spectra give only nine experimental values. But the substitution of the hydrogen atoms by deuterium gives six new compounds, C_2H_3D, $C_2H_2D_2$ (*cis*, *trans*, asymmetrical) C_2HD_3, C_2D_4, corresponding to the same potential function. Since each of these compounds gives nine new frequencies, $9\times7=63$ experimental values are obtained by this process for the determination of fifteen coefficients.

(2) BRIEF DISCUSSION OF THE THEORY

The symmetrical coordinate method, introduced by Manneback[2] for the calculation of molecular vibration frequencies, shows that in the case of C_2H_4 and C_2D_4 it is possible to classify into four groups the frequencies corresponding to the planar motions of the molecule. The first group S_1[3] corresponds to the 3 symmetrical vibrations with respect to the two planes of symmetry, the second group S_2 corresponds to the two antisymmetrical vibrations with respect to the same planes, the third and the fourth group correspond to the two vibrations A_1 and A_2 symmetrical with respect to one of these planes and antisymmetrical with respect to the other. S_1 and S_2 are Raman active and inactive in the infra-red. A_1 and A_2 are Raman inactive and active in infra-red. In the case of $C_2H_2D_2$ (*trans*), a center of symmetry permits a separation of the frequencies into two groups, one symmetrical and the other antisymmetrical with respect to the center. $C_2H_2D_2$ (*cis* and asymm.) can also be divided into two groups π and σ, symmetrical and antisymmetrical with respect to their planes of symmetry. The asymmetrical compounds C_2H_3D and C_2D_3H have no symmetry at all, and no separation is possible.

(3) PREPARATION OF COMPOUNDS

The ethylenes were prepared in two different ways. The first method employs the exchange of hydrogen atoms between ethylene and heavy water, by means of a catalyst.[4] One can, thus, by substituting new quantities of heavy water for that impoverished by the exchange, obtain a gradual enrichment of deuterium atoms in the ethylene. The monosubstituted ethylene appears first. It is gradually supplanted by the disubstituted forms, which themselves are finally transformed into the trisubstituted and tetrasubstituted ethylenes. We prepared two different samples by the method of exchange reaction. The

[1] G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. London **A148**, 250 (1935). J. M. Delfosse, Ann. Soc. Scient. **B55** (1935). L. G. Bonner, J. Am. Chem. Soc. **58**, 34 (1936). C. Manneback and Verleysen **B56**, 349 (1936). A. Verleysen and C. Manneback **B57**, 31 (1937).

[2] C. Manneback, *Calcul et identification des molécules* (Liège, 1935).

[3] The notation throughout this paper is the same as that employed by Manneback and Verleysen (reference 1).

[4] J. Horiuchi and Polanyi, Trans. Faraday Soc. **30**, 1164 (1934).

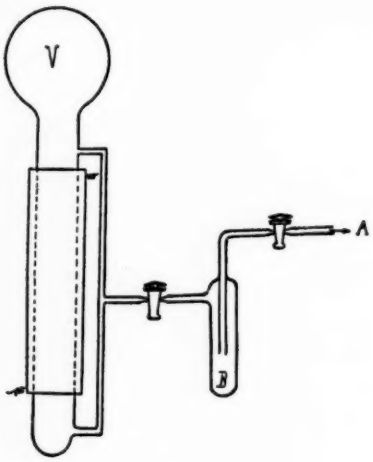

FIG. 1.

heavy water employed was 99.6 percent pure. The light ethylene used for the exchange process was prepared by the ordinary method of dehydrating alcohol by sulfuric acid. It was prepared separately for each of the exchanges and carefully distilled. For the first exchange, we made use of a catalyst prepared by the precipitation and calcination of nickel hydroxide by ammonia on pumice. The catalyst was then reduced in the apparatus employed for the reaction, at a temperature of 350 degrees, by a stream of hydrogen. The hydrogen was pumped out and a sample of heavy water, (5 g) introduced in trap *A* (Fig. 1), was carefully outgassed and then distilled into trap *B*. The ethylene was then introduced into the vessel *V* and the heavy water distilled into the same vessel. The apparatus was constructed in such a way that the constituents would be thoroughly mixed. The mixture was then heated at 100 degrees for several days, after which the ethylene was examined. Then it was reacted again with a new sample of heavy water. The first sample of ethylene was subjected to three exchanges. The results are represented by the microphotometer curves *a*, *b*, *c*. In the second case, 6 liters of ethylene at one atmosphere, were exchanged with 15 g of heavy water. The catalyst employed was an industrial one, generously furnished us by Professor H. S. Taylor. The mixture was heated at 150 degrees during several days. In addition, we have been able to prepare certain deutero-ethylenes in the pure state. The compounds thus obtained were:

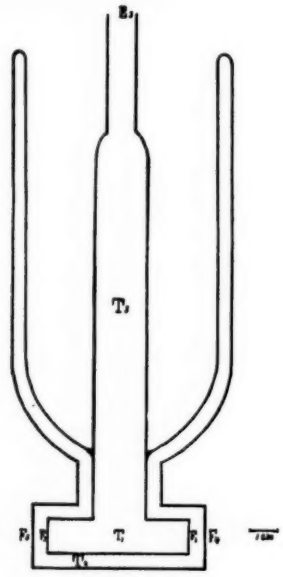

FIG. 2.

C_2H_3D, a mixture of $C_2H_2D_2$ (*cis* and *trans*), and C_2D_4. These compounds were prepared by reducing the corresponding ethylene dibromide with zinc in light water solution. In order to obtain the dibromide, we started with vinyl bromide and heavy hydrobromic acid in the first case, heavy acetylene and light hydrobromic acid in the second case, and finally, heavy acetylene and heavy hydrobromic acid.

$$\left.\begin{array}{ll} CH_2=CHBr+DBr & CH_2Br-CHDBr \\ CD\equiv CD+2HBr & CHDBr-CHDBr \\ CD\equiv CD+2DBr & CD_2Br-CD_2Br \end{array}\right\}+Zn$$

$$CH_2=CHD$$
$$CHD=CHD$$
$$CD_2=CD_2.$$

The vinyl bromide employed is a Fraenkel product. The hydrobromic acid was obtained by the action of water on phosphorous pentabromide distilled in vacuum. The acetylene was obtained by passing heavy water vapor over commercial calcium carbide at ordinary temperature. The carbide had previously been heated at 500 degrees for several hours in order to dry it. The synthesis of dibromide was slow in the first case. In the other two cases, it was necessary to accelerate the reaction by illuminating the product with ultraviolet light ($\lambda > 3300$A). Since the ethylenes were obtained by two different

TABLE I. (cm^{-1}).

C_2H_3D	$C_2H_2D_2$(*cis, trans*)	C_2D_4
1599.5 (12)	1567.3 (20)	1514.7 (15)
3014.9 (7)	3046.7 (1)	2251.6 (15)
2266.2 (5)	3033.1 (1)	981.6 (1,5)
1395.7 (9)	2290.7 (8)	2306 (0,2)
1286.4 (8)	2276.0 (8)	2272.6 (1)
2964.2 (3)	1215.0 (7)	2215.4 (0,8)
3007.6 (1)	1282.2 (7)	995.8 (2)
1340.3 (6)	763.4 (0,2)	1215 (0,1)
1619.2 (2)	863.4 (0,2)	1283.4 (0,6)
	2216.7 (0,4)	1567.3 (4)
		1544.3 (4)
24276	22793	24835
22794	22276	23534
21511	22235	21893
21501	22460	21438
		21376

TABLE II. $C_2H_4+C_2H_2D_2$ (cm^{-1}).

FIRST EXCHANGE	SECOND EXCHANGE	THIRD EXCHANGE
		981.0 (0,1)
		994.4 (0,1)
		1215.1 (0,7)
		1282.7 (0,4)
1286.0 (1)	1286.3 (0,5)	
1341.0 (13)	1341.3 (1)	1340.9 (0,1)
		1379.1 (0,5)
1397.5 (5)	1397.7 (0,5)	1397.3 (0,1)
		1514.4 (0,3)
	1544.3 (0,4)	1544.7 (4)
1567.3 (1,5)	1567.4 (2)	1567.3 (3)
	1581.2 (0,3)	1581.6 (1)
1600.7 (10)	1600.2 (1)	1600.4 (2)
1620.8 (15)	1621.0 (0,7)	
		2213 (0,2)
		2221.0 (0,2)
		2252.0 (0,1)
2266.2 (2)	2266.6 (0,3)	2266.8 (0,1)
		2273 (0,3)
		2291.4 (0,1)
2965.8 (5)	2966.0 (0,8)	2965.0 (0,4)
3007.1 (7)	3007.0 (3)	3006.8 (0,05)
3015.6 (6)	3015.3 (1)	3015.7 (0,05)
21817		
21833		
21622		

methods, it was possible to classify the lines unambiguously and to eliminate the lines arising from impurities.

(4) RAMAN SPECTRA OF THE PRODUCTS

(a) Technique

Light from two mercury vapor lamps operating at 3.8 amp. and 120 volts was converged on a cylindrical tube containing the liquefied gas by means of two condensers (132 mm in diameter). The tube was arranged parallel to the lamps. The optical system employed a diaphragm placed close to the tube in order to use the maximum amount of scattered light and eliminate light reflected by the walls of the tube. The image of the diaphragm was focused without magnification on the slit of the spectrograph by means of a lens. A three-prism Cojan spectrograph of aperture f:6 was employed. The dispersion of the instrument in the region of 4100A is 7A per mm. We used "Superguil" plates, with a sensitivity of 2100 HD. Exposure times of 40 hours were necessary to bring out the weak lines. In spite of these long exposure times, no lines corresponding to the non-planar vibrations were detected. The Raman flask consists of a cylinder T_1 closed by two polished quartz windows F_1 and F_2. Another tube T_3 is sealed to T_1. A tube T_2 concentric to T_1 is also closed by two quartz windows F_3 and F_4. Finally, a Dewar vessel is joined on as shown in Fig. 2. The gas introduced at E_3 is liquefied in tube T_3, runs into tube T_1 and is kept at a temperature sufficiently low so that it remains liquefied. The Raman lines were measured with a

TABLE III. (cm^{-1}).

	C_2H_4 exp.	C_2H_3D* theor.	C_2H_3D* exp.	$C_2H_2D_2$ (*cis*) theor.	$C_2H_2D_2$ (*cis*) exp.	$C_2H_2D_2$ (*trans*) theor.	$C_2H_2D_2$ (*trans*) exp.	$C_2H_2D_2$ (asymm.) theor.	$C_2H_2D_2$ (asymm.) exp.	C_2HD_3 exp.	C_2D_4 theor.	C_2D_4 exp.
ν_1	1620.1	1570.2	1600.2	1516.2	1567.3	1514.2	1567.3	1555.3	1581.4	1544.4	1428.0	1514.5
ν_2	3007.3	3030.5	3015.3	3065.0	3046.4	3049.2	3033.1			2272.6	2283.9	2251.8
ν_3	1340.7	2254.7	2266.4	2304.2	2290.1	2291.1	2275.9	2221.0	2221.0	2215.0	1008.9	981.3
ν_4		1380.3	1396.6	1247.2	1282.2	1240.2	1215.0	1357.8	1379.1	995.2		
ν_5		1261.8	1286.2	752.7	763.4	807.9	863.4					
ν_6		2986	2964.7								2308	2306
ν_7	944.0										758.3	780
	3072.0											

* The theoretical frequencies of C_2H_3D have been calculated by C. Lemaitre, Y. L. Tchang and C. Manneback. (C. Lemaitre, Y. L. Tchang and C. Manneback, Ann. Soc. Scient. **B121** (1937)). Recently Tchang, correcting the potential function for the anharmonicity, obtained theoretical frequencies which fit the experimental data with an error less than 0.5 percent. (In publication: Ann. Soc. Scient. Bruxelles.)

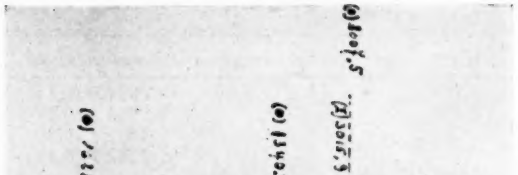

FIG. 3(a). First exchange.

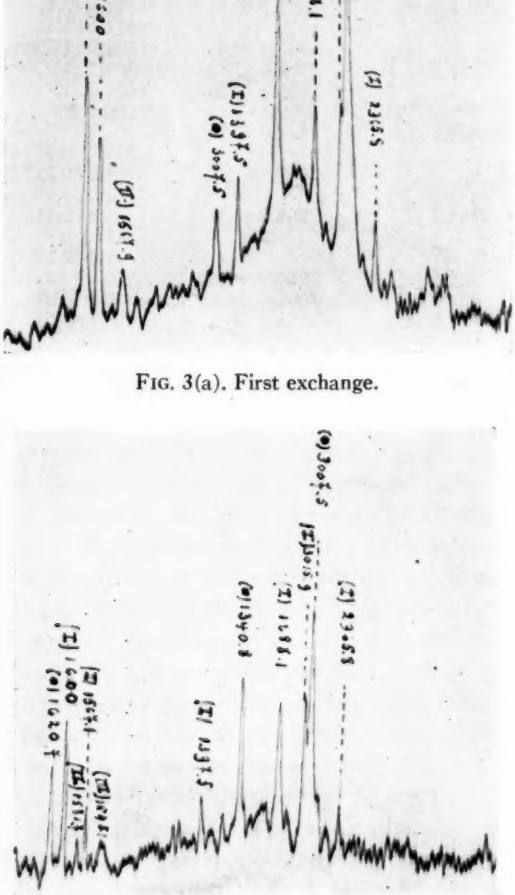

FIG. 3(b). Second exchange.

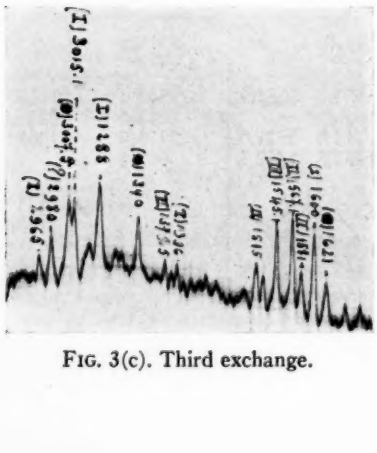

FIG. 3(c). Third exchange.

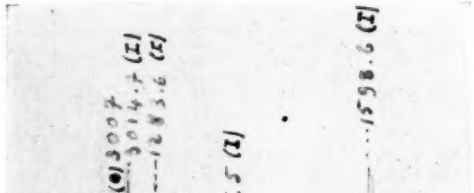

FIG. 3(d). C_2H_3D.

comparator by using an iron spark spectrum for comparison.

The results are given in Tables I–III. Tables I and II give directly the frequencies between the measured Raman lines, while the numbers in parenthesis indicate their relative intensities. Each of them comes from at least two different lines, and the mean value has been taken. The parent lines are:

27388.0 27354.4 24705.4 22938.0 (cm^{-1}).

Table I gives the lines corresponding to the spectrum of C_2H_3D, $C_2H_2D_2$, C_2D_4 prepared in the pure state. At the bottom of the table are given several weak lines for which we have not yet found satisfactory explanation. Table II gives the lines corresponding to the three different exchanges. Table III gives the classification of all the frequencies of vibration and a comparison with the theoretical predictions.

(5) IDENTIFICATION OF FREQUENCIES

Because of the use of not absolutely pure heavy water, the C_2D_4 and the $C_2H_2D_2$ contain a few percent of C_2HD_3 and C_2H_3D, respectively. Some lines of C_2HD_3 appearing also in the spectrum of $C_2H_2D_2$ can be explained by the presence of some heavy water remaining in the

C_2D_2 and giving exchange with HBr. Thus, the classification of frequencies needs careful consideration. To this end we are helped by the variation in intensities of the lines obtained in the successive exchange processes. After the first exchange, Fig. 3(a), the lines of C_2H_3D are visible, as shown in the microphotometer curve (a). The other two exchanges, Figs. 3(b) and (c), show an increasing intensity of the lines of C_2H_3D and a decreasing intensity of the lines of C_2H_4. At the same time, the lines of $C_2H_2D_2$ appear (microphotometer curves *b* and *c*). Another exchange using a large excess of heavy water gives all the compounds. From the equal intensities of the corresponding C_2H_4 and C_2D_4 lines, as well as those arising from C_2H_3D and C_2D_3H, it is obvious that the proportion of $C_2H_2D_2$ has reached a maximum. Therefore, the spectrum will give most information about the $C_2H_2D_2$ compounds. Finally, we shall use the theoretical prediction about the numerical values of the frequencies, their intensities and their depolarization factors. For example, the *A* frequencies of $C_2H_2D_2$ (*trans*) are forbidden in Raman effect by the selection rules. With regard to $C_2H_2D_2$ (*cis* and asymm.), all the frequencies are allowed, but the π are more intense than the σ ones. Using the different criteria, it has been possible to classify all the observed lines.

C_2H_4

This compound has been investigated by many authors. Its lines are very well known and we obtain:

3007.3 3072.0 1620.1 1340.7 944.0.

C_2H_3D

This compound contains a small amount of the light ethylene, whose lines are well known (microphotometer curve *d*). The frequencies obtained for C_2H_3D are:

1600.2 3015.7 2964.7 1396.6 1286.2 2266.4 3104.

This assignment is confirmed by the presence of all these lines in the spectrum of the first exchange, the decrease of their intensities in the following exchange, and by comparing their numerical values with the theoretical ones given by Manneback and Verleysen.

C_2D_4 and C_2D_3H

The lines of C_2D_3H are visible but very weak in the spectrum of C_2D_4 prepared from ethylene-d_4 dibromide. On the other hand, they are found together with those of C_2D_4 in the spectrum of the third exchange, but in the latter case their relative intensities are reversed. This reversal is very useful in making the classification. For instance, the 1514.5 line, four times more intense than the 1544.4 one in the C_2D_4 spectrum, is ten times less intense in the spectrum of the third exchange. 1514.5 is therefore one C_2D_4 line and 1544.4 one C_2D_3H line. The same method has been used to classify the other lines. We obtain:

C_2D_4 : 1514.5 2251.2 981.2 780.0 2304
C_2D_3H : 2215.0 2272.6 1544.4 995.2.

$C_2H_2D_2$ (*cis* and *trans*)

In the spectrum of $C_2H_2D_2$ prepared from ethylene-d_2 dibromide, the strongest lines of C_2D_4, C_2D_3H, C_2H_3D and C_2H_4 appear very weakly, the other lines are found in the exchange spectrum with expected intensities, and we find:

2275.9 2290.0 3033.3 3046.4 763.4
863.4 1215.0 1282.2 1567.3.

The 1282.2 line cannot be mistaken for any C_2H_3D line, because the strongest line in C_2H_3D, 1600, does not appear. In the same way $\nu_3=2275.9$ is different from $\nu_2=2272.6$ found in C_2D_3H, because $\nu_1=1545.4$ four times more intense than 2272.6, should also appear but does not. The 1567.3 is extremely strong and its first harmonic is very intense. This frequency corresponds to a vibration of the CHD groups against one another, and it is plausible that this vibration should be the same for $C_2H_2D_2$ (*cis* and *trans*). With regard to the other frequencies, the discrepancy between our results and the prediction of Manneback and Verleysen is so great that no classification is possible. However, if we observe that the product of the *cis* frequencies divided by the product of those of the *trans*, has a theoretical value of $[0.900816]^{\frac{1}{3}}$ we can choose a combination of the ten frequencies in such a way that the ratio

$$\frac{\omega_1^2\omega_2^2\omega_3^2\omega_4^2\omega_5^2}{\omega_1'^2\omega_2'^2\omega_3'^3\omega_3'^4\omega_3'^5}=0.900816 \qquad (1)$$

agrees best with the theoretical value. We find:

$$\left[\frac{1567\times3046\times2290\times1282\times763}{1567\times3033\times2276\times1215\times863}\right]^2=0.88974.$$

The relation (1) is rigorous only for harmonic motion, but it may be observed that the anharmonic correction shifts the *cis* and *trans* frequencies by the same amount. Therefore, the left member remains quite constant.

$C_2H_2D_2$ (asymmetrical)

This compound has not been obtained in the pure state, and it appears only in the exchange spectrum. The lines of the other compounds are well known. Hence we find:

1581.4 1379.1 2221.0.

(6) Discussion of Results

Table III gives the comparison between the experimental values and those calculated by Manneback and Verleysen. The frequencies corresponding to the motion of the radicals against each other are a good illustration of the Rayleigh law concerning the increasing frequency of a vibrating system accompanying the decreasing mass of one part of the system. If we consider these frequencies, as coming from a diatomic molecule, the mass of each atom being the mass of the corresponding radical, it is to be observed that for $C_2H_2D_2$, C_2H_4, C_2D_4, they rigorously obey the following formula

$$\nu^2=\kappa F/\mu,$$

where $F=10.796$ dynes/cm; μ is the reduced mass and κ a constant.

These frequencies are: 1514.5 (C_2D_4), 1544.5 (C_2HD_3), 1567.3 ($C_2H_4D_2$ *cis trans*), 1581.4 ($C_2H_2D_2$), 1600.2 (C_2H_3D), 1620.1 (C_2H_4). Manneback and Verleysen observe that the value of the high frequencies ν_1 and ν_3 of the disubstituted isomers are each approximately equal to the arithmetic mean of two high frequencies which combine to give the mode of vibration under consideration. One of these pairs of high frequencies arises from C_2H_4 and the other from C_2D_4. For example, the motion corresponding to the frequency (*trans*) ν_2 in which the D atom does not move, can be thought of as the superposition of the ν_2 and ν_6 frequencies in C_2H_4. Therefore the motion is not much influenced by the substitution of H by D. In the same way, the vibration of $C_2H_2D_2$ (*trans*) ν_3 can be represented by the superposition of the ν_2 and ν_6 vibrations of C_2D_4. The frequencies must have the following values,

$$\tfrac{1}{2}(3007.3+3072)=3039;\quad \tfrac{1}{2}(2251+2304)=2277.$$

By a similar argument, we find for ν_2 (*cis*) and ν_3 (asymm.) the following formula:

$$\tfrac{1}{2}(3007+3107)=3057;\quad \tfrac{1}{2}(2251+2193^5)=2221$$

as compared with the experimental values: 3046 and 2221. We can also expect for the infra-red frequency of C_2D_4 the approximate value:

$$2329=2\times2290-2251.$$

The discrepancy between the experimental values seems to be due partly to the anharmonicity. It is easy to show how important this correction is. The ratio between the product of C_2H_4 and C_2D_4 frequencies belonging to the same symmetry group, supposing the vibration to be harmonic, is:

$$\omega_{1H}\omega_{2H}\omega_{3H}/\omega_{1D}\omega_{2D}\omega_{3D}=1.998;$$
$$\omega_{6H}\omega_{7H}/\omega_{6D}\omega_{7D}=1.666.$$

Substituting experimental values we find:

$$\frac{1621.1\times3007.3\times1340.7}{1514.5\times2251.2\times981.2}=1954;$$

$$\frac{3072\times944}{2304\times780}=1.623.$$

The anharmonicity correction is thus of the order of 2 percent for the S_1 group and 3 percent for the S_2 group.

In conclusion we wish to thank G. Maes for his constant assistance during the course of these experiments.

[5] This value has been found by Sutherland. See G. B. B. Sutherland and G. K. T. Conn, Nature **140**, 644 (1937).

The Mercury Photosensitized Hydrogenation of Ethylene, Ethylene-d_4 and Partially Deuterized Ethylenes

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(Received March 10, 1938)

The hydrogenation of ethylene, ethylene-d_4 and partially deuterized ethylene photosensitized by excited mercury to $\lambda=2537$A has been studied. It has been found that the rate of hydrogenation of the deutero-compound is more rapid than that of ethylene under comparable conditions. With excess hydrogen, the rate is independent of the ethylene pressure. The data obtained indicate that butane is the important product together with small amounts of ethane relatively more abundant in the case of ethylene-d_4. Negligible amounts of methane are formed. The suggested mechanism involves the reactions $H+C_2H_4=C_2H_5$ followed by $C_2H_5+C_2H_5=C_4H_{10}$ and to a lesser degree, $C_2H_5+C_2H_5=C_2H_6+C_2H_4$. At low hydrogen concentrations, or in absence of hydrogen, a photosensitized polymerization occurs, faster with ethylene than with ethylene-d_4. The slower rate of polymerization of the deutero-compound may be explained on the basis of zero-point energy differences between C_2H_4 and C_2D_4 in their reactions with free radicals to yield more complex radicals.

THE present investigations were begun in the hope that comparative studies of the mercury photosensitized hydrogenation of ethylene and ethylene-d_4 might assist in the solution of problems which remained unsolved in the earlier investigations with ethylene alone.[3] The changes in reaction velocity that result from the use of deutero-compounds in place of hydrogen compounds might serve to indicate the nature of the intermediate stages in the over-all processes observed. The analysis of these stages can be more penetratingly effected now, by reason of our increased knowledge of the kinetic characteristics of the atomic and free radical constituents of systems so produced.[4] The accuracy of such kinetic characteristics can, in turn, be checked by the newer data.

EXPERIMENTAL

Light source

As source of resonance radiation we have employed the Hanovia quartz mercury vapor, rare gas discharge tube, Sc 2537, operating, from a 220 a.c. volt primary, at 5000 volts and 100 milliamperes by means of a suitable transformer. The lamp was a double-U in shape each loop about 15 cm length in leg. Satisfactory operation was secured only when one of the electrodes was kept cooled to constant temperature in a stream of running water. This served to maintain a constant mercury vapor pressure and to prevent clouding of the arc tubing by deposit of mercury on the walls from which radiation entered the reaction system. It was also found that variations in intensity of resonance radiation resulted as the transformer heated up when in use, so that the arc system was operated for a period of time before each experiment so that equilibrium might be established.

Gases

The ethylene used was prepared in two ways (*a*) by the reaction of zinc metal on ethylene dibromide in water solution and (*b*) by the action of sulphuric acid on ethyl alcohol. It was purified by passage through alkali and concentrated sulphuric acid and then submitted to fractional distillation. The results were the same on the two samples.

Deutero-ethylene, kindly placed at our disposal by Professor M. de Hemptinne, was obtained by the action of zinc metal on ethylene dibromide-d_4 obtained by the addition of deuterium bromide to deutero-acetylene. It was purified by the usual method and by a fractional distillation and allowed finally to react with metallic sodium to remove any traces of halogen compounds. The sample contained 95 percent C_2D_4 as determined by measurements of Raman spectra.[5] A partially deuterized ethylene, also studied, was obtained

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[2] Francqui Professor, 1937, University of Louvain.
[3] See, for example, H. S. Taylor and D. G. Hill, J. Am. Chem. Soc. **51**, 2922 (1929).
[4] J. C. Jungers and H. S. Taylor, J. Chem. Phys. **4**, 94 (1936); K. Morikawa, W. S. Benedict and H. S. Taylor, ibid. **5**, 212 (1937).
[5] de Hemptinne, Jungers and Delfosse, J. Chem. Phys., **6**, 319 (1938).

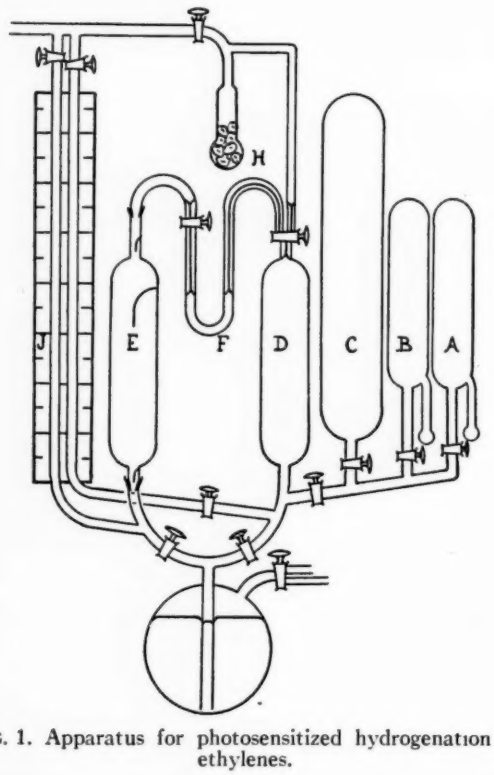

FIG. 1. Apparatus for photosensitized hydrogenation of ethylenes.

by equilibration of ethylene and deuterium oxide on an active nickel catalyst at a temperature of 150°C. The Raman spectra showed that the sample was approximately 50 percent D and contained principally the *cis* and *trans* forms of symmetrical $C_2H_2D_2$, with a little $CH_2=CD_2$ and also small amounts of C_2D_3H and C_2H_3D.

The hydrogen was prepared by electrolysis, freed from oxygen over platinized asbestos and from water vapor in a liquid-air trap and over phosphorus pentoxide. Another sample was further purified by adsorption and desorption from charcoal. No variations in reaction due to method of purification were noted.

Apparatus

The experimental arrangement is shown in Fig. 1. The vessels *A*, *B* and *C* are reservoirs for the gases, *A* and *B* being provided with a side tube in which the ethylenes could be frozen out with liquid air and any noncondensible gases removed by pumping. The reservoir *B* for deutero-ethylene contained metallic sodium. Mixtures of hydrogen and one of the ethylenes in variable concentrations could be introduced into the cylindrical quartz reaction chamber *E* (19 cm×2.3 cm diameter) after an appropriate mixture had been secured in *D*. Evacuation of the system was effected through the tubes *J* which could also serve as a manometer, The U-tube, *F*, between *D* and *E* could be used to freeze out the condensible gases in liquid air. The uncondensed gas (H_2+CH_4) could then be pumped off by means of *D* and compressed on to the copper oxide tube *H*, the unburnt residue, methane, being then measured in *E*. The condensible gases, after pressure measurement, could be similarly burned in *H* and the residual CO_2 measured in *E* by pressure measurement before and after liquid air was applied to *F*.

In certain experiments a filter of acetic acid solution, 25 percent by volume, was employed. This was discarded after it had been shown that the radiation from the lamp was so very largely monochromatic ($\lambda=2537$A) and that polymerization and reaction due to straight photochemical action was negligible.

EXPERIMENTAL RESULTS

In a preliminary series of some fifty experiments a number of facts were ascertained with respect to the reactions occurring in the experimental arrangement already described. The quantitative data are not given because they lack intercomparability due to incomplete attainment of uniform operating conditions. The variations of intensity due to the transformer and mercury deposition inside the arc system have already been noted. It was also found that the velocity of reaction was also very sensitive to the mercury vapor content of the air between the arc and quartz reaction vessel. During the night in a closed laboratory the mercury vapor concentration of the laboratory air increases to such a degree that initial reaction velocities are slow due to absorption of resonance radiation outside the reaction vessel. On operating the arc this mercury is slowly removed by photosensitized oxidation and the reaction velocity in the hydrogen-ethylene system correspondingly increases. Ventilation of the room by clean air from the outside produced a similar acceleration due to removal or decrease of mercury vapor.

From this series of experiments the following conclusions could certainly be drawn. The reac-

tion proceeded steadily until all the ethylene was consumed at which point the pressure change ceased abruptly. At this point it was always found that the pressure of condensible gas in the residue was about one-half of the ethylene pressure admitted. This points to the production not of ethane but of butane. That the product was not ethane was shown by combustion over copper oxide. The carbon dioxide formed corresponded to a hydrocarbon between C_3H_8 and C_4H_{10}. Further, the bulk of the gaseous product condensed in liquid air was also condensible in melting ethyl acetate (m.p. $= -82.4°C$) at which temperature ethane has a vapor pressure of >760 mm. This observation is true for deutero-ethylene reactions as well as for ethylene, the pressure of gases condensible in liquid air being slightly higher in the deutero-ethylene case. Here also, however, combustion pointed to a product with a formula between C_3 and C_4. This result was obtained irrespective of variations in concentration ratio, pressures or velocity of reaction (intensity). In this respect it is in disagreement with the earlier results of Taylor and Hill.[3] In their experiments with concentrations of hydrogen up to 50 percent, saturated hydrocarbons with composition between C_3 and C_4 were frequently obtained, but with higher hydrogen concentrations the saturated product approached more and more to C_2. One possible explanation of the discrepancy is suggested by the observation that, in the present series of experiments, it was never possible to show the formation of any important amount of methane. The highest recorded methane pressure in the preliminary series was 0.05 cm with hydrogenations of ethylene within the pressure range 1–11 cm. Taylor and Hill[3] continuously found marked amounts of methane, especially when reaction was prolonged beyond the end-point as recorded by pressure change. It would appear that this methane arose in part, if not wholly, from interaction of atomic hydrogen with polymeric products $(CH_2)_n$ always laid down by prolonged illumination in presence of excited mercury. Indeed methane and $(CH_2)_n$, a liquid polymer, are the final products of prolonged illumination of any hydrogen-hydrocarbon mixture, saturated or unsaturated, with excited mercury. In hydrogen rich mixtures, especially with a reaction vessel covered internally with (CH_2) polymer, methane formation is increasingly possible. In the present experiments any such deposit was removed after each experiment by oxidation with air at the high temperature of the blowpipe flame. We, therefore, conclude that in clean vessels the predominant saturated product is butane C_4H_{10}.

Quantitative data

The quantitative results were obtained in a continuous series of experiments over a period of forty hours where all conditions controlling uniformity of operation were carefully observed. All these experiments were carried out in the reaction vessel covered with mercury droplets on the side opposite to that through which the light entered, in order to secure continuous saturation

TABLE I. *Influence of ethylene and of hydrogen concentrations on their photosensitized interaction.*

No. of Expt.	P_{H_2} cm	$P_{C_2H_4}$ cm	ΔP cm	C.G. cm	t' in min.	Time in min.	Nature of Ethylene
Influence of Ethylene Concentration							
29	30.10	10.03	9.97	5.36	28	53	D
30	30.02	10.00	9.98	4.86	34	66	H
31	30.34	4.99	4.97	2.71	13.5	26	D
32	30.41	4.98	5.02	2.39	15.5	31	H
33	30.08	2.89	2.98	1.36	10.0	20	H
34	30.15	2.96	3.02	1.49	7.5	16	D
37	5.14	3.00	3.05	1.36	14.2	28	H
38	5.28	2.98	2.94	1.76	11.7	23	D
39	5.08	0.98	0.93	0.56	5.5	11	D
40	5.18	0.98	1.01	0.54	8.5	16	H
Influence of Hydrogen Concentration							
33	30.08	2.89	2.98	1.36	10	20	H
34	30.15	2.96	3.02	1.49	7.5	16	D
35	15.28	2.96	2.94	1.68	8.7	17	D
36	15.42	2.96	2.93	1.49	10.7	21	H
37	5.14	3.00	3.05	1.36	14.2	28	H
38	5.28	2.98	2.94	1.76	11.7	23	D
41	2.00	2.96	2.97	0.97	23.5	40	H
42	2.12	2.96	2.86	1.50	20.7	35	D
43	0.77	3.00	2.71	——	45.7	65	D
44	0.75	2.99	2.85	——	38.5	60	H
45	0.00	2.94	2.68	——	51.5	70	H
46	0.00	2.96	2.35	——	75.0	90	D
Influence of Deuterium Content							
106	14.98	2.98				19	HD
107	15.09	2.97			9.8	21	HD
111	——	2.98			62.5		HD
112	——	2.97					HD

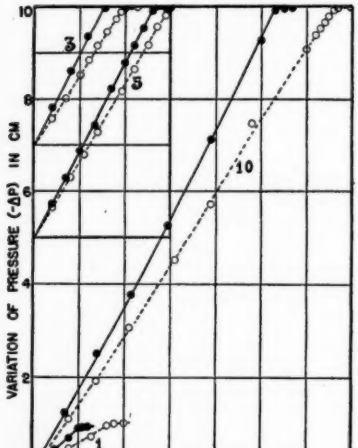

FIG. 2. Velocity of hydrogenation at varying ethylene pressures. $P_{H_2}=30$ cm. $P_{C_2H_4}=1$, 3, 5 and 10 cm. Open circles, C_2H_4; filled circles, C_2D_4.

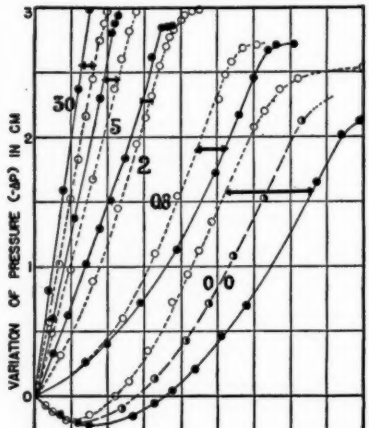

FIG. 3. Influence of hydrogen pressure at constant ethylene pressure (3 cm). $P_{H_2}=30$, 5, 2, 0.8 and 0.0 cm. Filled circle, C_2D_4; half-filled circle, $C_2H_2D_2$; open circle, C_2H_4.

of the reaction mixture with mercury vapor. The forty-hour period of experiments succeeded a period of one day in which the arc was operated to secure a steady state. The data secured in these runs are tabulated in Table I and shown graphically in Figs. 2 and 3. The first ten experiments show the influence of variation in ethylene concentration at two hydrogen pressures 30 and 5 cm. The final twelve experiments concern the influence of variation in hydrogen pressure at an ethylene pressure of $\sim$3 cm. The final column shows whether the ethylene studied was C_2D_4(D) or C_2H_4(H). The preceding column shows the times t at which reaction, as measured by pressure change, was complete. In the last four experiments this time is uncertain, as can be seen from Fig. 2, the process occurring being predominantly polymerization. The sixth column gives the time t' required to produce a decrease in pressure equal to one-half the initial pressure of ethylene. For the reactions with high ethylene content this is not equal to the time of half-reaction since in these cases the change in pressure was not equal to $P_{C_2H_4}$. The column headed C.G. confirms the result obtained in the preliminary experiments that the condensible residue is approximately one-half the pressure of the ethylene consumed, somewhat greater with deutero-ethylene than with ethylene. The concordance of the columns $P_{C_2H_4}$ and ΔP shows that the pressure change is equal to the ethylene pressure within the experimental error, for mixtures rich in hydrogen.

The velocity data for the same experiments are presented graphically in Figs. 2 and 3. It is at once obvious that the hydrogenation of ethylene-d_4 is faster than the hydrogenation of ethylene. Only at very low hydrogen pressures when the predominant process is one of polymerization is the relation reversed, the polymerization of ethylene-d_4 being slower than that of ethylene.

With mixtures of 15 cm hydrogen and 3 cm $C_2H_2D_2$ the reaction was complete in 19 minutes exactly intermediate to the times recorded in experiments 35 and 36 for the corresponding reaction mixtures with C_2D_4 and C_2H_4. As shown in Fig. 3, the rate of polymerization of $C_2H_2D_2$ is also approximately the mean of those of C_2H_4 and C_2D_4. Since the method of preparation of $C_2H_2D_2$ was entirely different from that of the other two ethylenes, these results indicate that the divergences in rate between the proto- and deutero-ethylenes are not due to fortuitous impurities but are determined by the extent of deutero-substitution.

DISCUSSION OF RESULTS

The results of this research clarify considerably the problem of mercury sensitized hydrogenation of ethylene when compared with the data of

previous work. It is now evident that, in clean quartz reaction vessels, with sufficient hydrogen present, the predominant product is butane. In no other way can the ratio of condensible gas in the product to ethylene reacted be explained. Several alternatives are exhibited by the following equations:

$$C_2H_4+H_2=C_2H_6 \qquad \text{C.G.} : \Delta P=1 : 1$$
$$2C_2H_4+H_2=C_4H_{10} \qquad \text{C.G.} : \Delta P=1 : 2$$
$$C_2H_4=(CH_2)_n(\text{liq}) \qquad \text{C.G.} : \Delta P=0 : 1.$$

In each case $\Delta P=P_{C_2H_4}$ for complete reaction, and C.G. refers to gaseous product condensible in liquid air.

In the first eighteen experiments of Table I, the condensible gas, with ethylene, is in every case close to and actually slightly less than one-half of the ethylene disappearing. It would be surprising if this were due to a fortuitous combination of ethane and butane formation with the right amount of polymerization (to liquid $(CH_2)_n$) to give the observed ratio of $\frac{1}{2}$, especially with the wide ethylene : hydrogen ratios studied. With ethylene-d_4 the ratio of condensible gas to ethylene reacted is in every case somewhat larger than $\frac{1}{2}$ so that we must conclude that, in this case, there is a greater tendency to form ethane-d_4 than to form ethane from ethylene.

With $P_{H_2}=30$ cm and a ratio equal to or greater than $3H_2 : 1C_2H_4$ or C_2D_4 the velocity of hydrogenation with either isotopic ethylene is practically independent of the ethylene concentration, as can be seen from curves 3, 5 and 10 of Fig. 2. This points to a practically quantitative acceptance of the resonance energy of the mercury by hydrogen and consequent formation of atomic hydrogen. In these experiments therefore we may write the initial process as

$$H_2+Hg'\rightarrow HgH+H\rightarrow Hg+2H. \qquad (1)$$

To yield butane we suggest that this reaction is followed by

$$H+C_2H_4=C_2H_5, \qquad (2)$$
$$C_2H_5+C_2H_5=C_4H_{10}. \qquad (3)$$

The small yield of C_2H_6 is evidence that the reaction

$$C_2H_5+H_2=C_2H_6+H \qquad (4)$$

is of low probability and this agrees with previous estimates of the activation energy for reaction (4), $E>11$ kcal.[5, 6] The more probable reaction for the production of ethane is the disproportionation reaction,

$$C_2H_5+C_2H_5=C_2H_4+C_2H_6. \qquad (5)$$

Our ratios of condensible product to ethylene reacted would indicate that this reaction (5) is a little more probable when the radical is C_2D_4H than when it is C_2H_5. Since the product, in either case, is predominantly butane, reaction (3) would appear to have a smaller activation energy than reaction (5). This conclusion appears to be in conflict with some older work by Job and Emschwiller[7] on the photolysis of liquid ethyl iodide. They found predominantly ethane and ethylene with but little butane. This is probably due to the liquid phase conditions and more especially to complex reactions involving iodine atoms. We hope to control this result by studies in the vapor phase using a new technique recently developed by one of us for the photodecomposition of ethyl iodide to yield ethyl groups.[8] The data of Norrish and Appleyard[9] on the photolysis of methyl ethyl ketone vapor indicate that quite considerable association of the radicals to form ethane, propane and butane occurred. This points to reaction (3) rather than reaction (5).

The low production of ethane indicates also that the process

$$C_2H_5+H=C_2H_6 \qquad (6)$$

is not important in comparison with (3). We attribute this to a low stationary state concentration of atomic hydrogen compared with C_2H_5 which latter governs the rate of (3). We find the reason for this in the occurrence of reaction (2) consuming hydrogen atoms with formation of ethyl. The inhibitory action of ethylene in chain reactions involving radicals and atomic hydrogen is well known[10] and may be explained by the occurrence of reaction (2). We cite the almost negligible formation of methane as another evidence of low hydrogen atom concentration since these atoms, at ordinary temperatures, give

[6] Trenner, Morikawa and Taylor, J. Chem. Phys. **5**, 203 (1937).
[7] Job and Emschwiller, Comptes rendus **179**, 52 (1924).
[8] Jungers and Joris, Bull. Soc. Chim. Belg. **47**, 135 (1938).
[9] Norrish and Appleyard, J. Chem. Soc. 874 (1934).
[10] Staveley, Proc. Roy. Soc. **A162**, 557 (1937).

considerable C−C bond splitting with formation of methane.[6]

For similar reasons we assume that the following possible sequence for butane formation,

$$H+C_2H_4=C_2H_5, \quad (2)$$

$$C_2H_5+C_2H_4=C_4H_9, \quad (7)$$

$$C_4H_9+H=C_4H_{10}, \quad (8)$$

is less important than (2) and (3). That polymerization is a relatively slow process is suggested by our earlier work on ethylene polymerization, with methyl radicals from the photolysis of acetone,[11] where rapid reaction occurred only above 140°C. This is confirmed also by the experiments with ethyl iodide as the source of the radicals.[8] Also, if this sequence were the mode of production of butane we should not expect the hydrogenation of ethylene-d_4 to be faster than that of ethylene, a fact which is abundantly clear from all our data. For, reaction tion (7) is an essential step in the polymerization mechanism and our measurements with hydrogen absent or even in small concentrations clearly indicate that the polymerization of ethylene-d_4 is *slower* than that of ethylene. (Curves 00 of Fig. 3.)

The pairs of curves 30, 5 and 2 of Fig. 3 indicate that, at constant ethylene pressure, 3 cm, the velocity is very little dependent on the hydrogen pressure between the limits of 5 and 30 cm. Coupled with the practical independence of ethylene concentration, deduced from curve pairs 3, 5 and 10 of Fig. 2, this leads to the conclusion that with mixtures rich in hydrogen the hydrogenation process is practically zero order with respect to the two reactants.

With $P_{H_2}=5$ cm or less and $P_{C_2H_4}=1$–3 cm there is evidence that not all the resonance radiation is taken by the hydrogen. The rate of hydrogenation progressively decreases with decrease of hydrogen content and the character of reaction changes toward polymerization. When hydrogen is absent there is, in agreement with earlier findings,[12] first a pressure increase and then a decrease. The interval during which an increase is observed is more prolonged with ethylene-d_4 than with ethylene, which is in accord with the slower velocity of polymerization. The pressure increase has already been identified[12] with the initial formation of hydrogen and acetylene. In our experiments with low or zero hydrogen concentrations we have noted the yellow polymer, cuprene, characteristic of acetylene polymerization. We hope later to test whether the polymerization process may not always require small concentrations of hydrogen for its occurrence under these conditions of excitation by resonance radiation.

The quantitative anslysis of the velocity data would require measurements on the quenching efficiencies of the molecules of ethylene and ethylene-d_4. Neither of these have been studied. The small variations in the velocities of hydrogen rich mixtures, represented by the appropriate curves in both Figs. 2 and 3 can be approximately related with each other on the assumption that hydrogenation is determined by the resonance radiation absorbed by the hydrogen in the mixture of gases, the ethylenes quenching in proportion to their partial pressures with an efficiency somewhat less than that of hydrogen. It is known that the relative quenching efficiency of ethane is only of the order of 5 percent of that of hydrogen, but it is known also that the unsaturated hydrocarbons are more efficient than the saturated as quenching agents.[13] From the data it is not possible to decide whether there are material differences between the quenching efficiencies of ethylene and ethylene-d_4. The velocities obtained are also dependent on the rates of the two association reactions (2) and (3). The faster rate of hydrogenation with ethylene-d_4 would point to a greater probability of these processes with the deutero-compound than with ethylene. The slower rate of polymerization of the ethylene-d_4 is most readily interpreted on the basis of a larger energy of activation in the polymerization step (7), probably involving the zero-point energies of the molecules C_2H_4 and C_2D_4, respectively. We hope later to test this with free radicals from photodecomposition of organic molecules as the starting agents in the polymerization chain.

[11] H. S. Taylor and J. C. Jungers, Trans. Faraday Soc. **33**, 1353 (1937).

[12] Bates and Taylor, J. Am. Chem. Soc. **49**, 2438 (1927).

[13] Bates, J. Am. Chem. Soc. **52**, 3825 (1930); **54**, 569 (1932).

The Temperature Variation of Diffusion Processes

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The Eyring concept of holes in liquids and his theory of absolute reaction rates indicate that diffusion coefficients should vary exponentially with temperature. Data in the literature indicate that this is true. It is shown that empirical observations concerning the relation between diffusion velocity and its temperature coefficient, hitherto generally assumed to be linear, are readily explained upon the basis of holes in liquids as a controlling factor. As with viscosity, in liquids containing hydrogen bonds relatively high activation energies of diffusion are found. Data for small diffusing molecules should not show a constant diffusion-viscosity product as required by the Stokes-Einstein relation at constant temperature, but a product varying within restricted ranges with the dimensions of the solvent molecules. Data already available tend to confirm this conclusion.

THE concept of holes in liquid systems has been shown by Eyring[1] to lead straightforwardly to a theory of viscosity, plasticity and diffusion in condensed systems with the aid of the Eyring theory of absolute reaction rates.[2] The application of this theory of viscosity to a number of experimental data over a range of temperature and pressure has been examined by Ewell and Eyring[3] and the activation energy of the viscosity process related to the energy of vaporization of the liquid, by employing the relation, developed by Eyring and Hirschfelder,[4] between free volume and energy of vaporization.

In his original communication,[1] dealing with diffusion, Eyring pointed out that the diffusion coefficient D is

$$D=\lambda^2 k_1, \tag{1}$$

where λ is the average difference between two successive minima in the potential energy curve representing the flow of a diffusing molecule past a molecule of the medium, when both types of molecule are approximately the same size. The constant k_1 is the absolute rate of reaction for the transition. For ordinary viscous flow, it was shown that, to a sufficient approximation, the viscosity η could be represented by the equation

$$\eta=\lambda_1 kT(\lambda^2\lambda_2\lambda_3 k_1)^{-1}, \tag{2}$$

where λ_1 is the perpendicular distance between two neighboring layers of molecules sliding past each other, λ_2 the distance between neighboring molecules in the direction of flow and λ_3 the intermolecular distance in the plane normal to the direction of motion. In this way the relation between diffusion and viscosity, from Eqs. (1) and (2) becomes

$$D=\lambda_1 kT/\lambda_2\lambda_3\eta \tag{3}$$

for molecules of similar sizes. This is to be compared with the well-known relationship for the diffusion of very large molecules in a medium of smaller molecules,

$$D=kT/6\pi r\eta. \tag{4}$$

In the light of Eq. (3) Eyring examined the data of Orr and Butler for the diffusion of heavy into light water[5] at 0 and 45° and found that the results indicated that, in viscous flow, the plane of the water molecule tended to coincide with the plane of flow and that λ_1 the perpendicular dimension was the small one, equal to 1.44×10^{-8} cm whereas $(\lambda_2\lambda_3)^{\frac{1}{2}}$ had the value 4.54×10^{-8} cm. Eq. (4) leads to unreasonably small values of r. Eyring also emphasized that, for the diffusion of ions in solutions of electrolytes, Eq. (3) should normally be employed.

The variation of viscosity with temperature was tested by Ewell and Eyring by means of the approximate formula

$$\eta=1.090\cdot10^{-3}\frac{M^{\frac{1}{2}}T^{\frac{1}{2}}}{V^{\frac{2}{3}}\Delta E_{\text{vap}}}\exp\frac{\Delta E_{\text{vap}}}{nRT}, \tag{5}$$

where ΔE_{vap} is the heat of vaporization in calories per mole and n is a constant for a given substance

[1] H. Eyring, J. Chem. Phys. **4**, 281 (1936).
[2] H. Eyring, J. Chem. Phys. **3**, 107 (1935).
[3] R. H. Ewell and H. Eyring, J. Chem. Phys. **5**, 726 (1937).
[4] H. Eyring and J. Hirschfelder, J. Phys. Chem. **41**, 249 (1937).
[5] Orr and J. E. V. Butler, J. Chem. Soc. 1273 (1935).

(3–4) which can be interpreted as expressing the fraction $(1/n)$ of the heat of vaporization necessary for the production of a hole of suitable size for the flow process to occur. Diffusion therefore should show a similar exponential variation with temperature since it is related to viscosity by either Eqs. (3) or (4).

In the older treatments of diffusion in liquid systems[6] the data on the effect of temperature have normally been represented as a linear function of temperature and not as an exponential function even though, in contrast to viscosity, the subject of diffusion has generally been treated in sections dealing with reaction velocity in heterogeneous systems. This doubtless arises from the restricted material on temperature variation, measurements of the diffusion coefficient being often only available at two temperatures, the data being represented by an equation of the form

$$D_2/D_1 = 1+\alpha(T_2-T_1). \qquad (6)$$

In the precision measurements of Cohen and Bruins[7] on the diffusion of tetrabromethane in tetrachlorethane solutions, extended over the range 0–55°C it was found that the series of six measurements could not be represented by a linear interpolation formula and an equation in t and t^2 was derived by the method of least squares. These data of Cohen and Bruins form the best material with which to test the variability of diffusion with temperature. By plotting the logarithm of the mean diffusion constants against the reciprocal of the absolute temperature in the range above indicated, an excellent linear plot is obtained from which an activation energy of diffusion = 3490 calories can be derived.

Cohen and Bruins simultaneously determined with great precision the viscosity of the tetrachlorethane employed as medium, also representing their data over the same range of temperature by means of an equation with powers of t and t^2. Plotting the logarithm of the viscosity against the reciprocal of the temperature again yields an excellent straight line, whose slope, however, leads to a somewhat lower value for the activation energy of the viscosity process, 2995 calories. The molecular heat of vaporization of this compound has been determined from vapor pressure measurements of Herz and Rathmann[8] who found 9134 calories, giving a Trouton constant of 21.8 indicating a normal liquid. The relation between the activation energy of the flow process and the heat of vaporization leads to a value of $n=3.0$ in Eq. (5) in agreement with the viscosity results for $C_2H_4Cl_2$ and $C_2H_4Br_2$ examined by Eyring and Ewell. The same Trouton constant for tetrabromethane gives for the heat of vaporization at the boiling point ($T\sim515$°K) the value 11230 calories. Using the above value of $n=3$, the activation energy of the flow process in tetrabromethane would then be 3745 calories. It is significant that the activation energy of diffusion is fairly close to the mean of these two activation energies of viscous flow ($E_D=3490$; $\frac{1}{2}E_{vis}(-Cl_4+-Br_4)=3370$) suggesting that, in the diffusion process, the motion of the diffusing molecule past the medium molecule demands a free volume approximately the mean of that required by the two molecules in their separate viscous flows.

Other data expressing diffusion coefficients over a range of several temperatures are very meager. From the *International Critical Tables*[6] we select data on the diffusion of mannitol in aqueous solutions containing 0.3 gram moles per liter. These data[9] are the most extensive as to temperature range (0–70°) of those recorded. Plotting log D against $1/T$ over this range we obtain, not a straight line, but one slightly curved toward the $1/T$ axis. Calculation of activation energies from point to point over the temperature range shows a value for the activation energy decreasing steadily toward a constant value somewhat greater than 3000 calories.

$T=$	273	283	293	303	313	323	333	343
$E_D=$	6590	5530	4460	4230	4035	3900	3774.	

These values show the same trend noted by Ewell and Eyring[3] for the activation energy of viscous flow of water and accounted for, by them, on the basis of the hydrogen bond structure of the liquid. The actual values for the activation energy of diffusion are upwards of 1 kcal. larger than the activation energies of viscous flow at the same temperature which is readily under-

[6] See, for example, Taylor, *Treatise of Physical Chemistry*, second edition (1931), pp. 1022–1028. Also, *International Critical Tables*, Vol. 5, (McGraw-Hill and Co., New York, 1929), p. 63.

[7] E. Cohen and H. R. Bruins, Zeits. f. physik. Chemie **103**, 404 (1923).

[8] Herz and Rathmann, Chem. Zeits. **36**, 1417 (1912).

[9] Scheffer and Scheffer, Proc. Acad. Sci. Amsterdam, **19**, 148 (1916).

TABLE I. *Temperature coefficients and activation energies of diffusion.*

D(cm²/day)	2.4	1.2–1.1	0.2–0.1
α	0.018	0.025	0.040
D_{t+10}/D_t	1.20	1.28	1.48
E_D	2875	4070	6470

standable when the size of the diffusing mannitol molecule and its hydrogen bond forming capacity are borne in mind.

Recently some data have been obtained using the technique developed by Northrop and Anson,[10] using a porous glass disk to separate the two solutions. Cole and Gordon[11] employed this technique to measure the diffusion of copper sulphate in dilute solution into sulphuric acid solutions containing 0.1 gram equivalents of acid per liter. Measurements made at 283, 291 and 298°K give a fair linear plot, log D *vs.* $1/T$, from the slope of which an activation energy of 5140 cal. is derived. This value is to be compared with an activation energy of viscous flow of water in the same temperature range somewhat less than 5000 cal. The abnormally high values of these activation energies, approximately one-half of the heat of vaporization (~10 kcal.) is again to be accounted for by the hydrogen bond structure of the liquid. Similar data recently given by Anson and Northrop[12] at several temperatures in the range 278–295°K for the diffusion coefficients of 2*n* NaCl, 1*n* and 0.1*n* HCl into water also give, approximately, a linear relationship, log D *vs.* $1/T$, with slopes corresponding to activation energies of 5450, 4850 and 4760 cal., respectively.

Although the data for the temperature variation of diffusion coefficients are scanty, there are nevertheless in the generalizations from the data obtained at only two temperatures results which are at once comprehensible from the standpoint of diffusion as a velocity process depending upon hole formation in the liquid medium. Thus, Öholm[6] on the basis of data at two temperatures with a wide variety of media, pointed out that substances showing a high value for the diffusion coefficient always showed a small temperature coefficient (α in Eq. (6)) and *vice versa*. Öholm's generalization is exemplified in Table I.

This is exactly what is to be anticipated on the basis of Eyring's theory. The more slowly diffusing materials require larger holes than the fast-diffusing species and the activation energy to produce these holes is correspondingly greater. The generalization of Öholm for the diffusion process is identical with the observation of Kohlrausch on ionic mobility. The greater is the ionic mobility the less the temperature coefficient. Herein lies also the reason for the observation that, with increased temperature, the transport numbers of the ions all approach 0.5; for, the ions with values less than 0.5 at a given temperature will have a larger temperature coefficient of mobility than those greater than 0.5.

Riecke[13] in 1890 attempted to formulate a kinetic theory of diffusion in dilute solutions and obtained an expression for the diffusion coefficient,

$$D = \text{const. } (1/M)^{\frac{1}{2}} l,$$

where M is the molecular weight and l the mean free path. Values for l of the order of 0.1A were obtained with this equation. That it cannot have real validity is evident from a selection of data compiled by Öholm in which diffusion coefficients for molecules with molecular weights between 50 and 300 showed entirely random variations on the molecular weight basis. Certain of these data are shown in Table II for 1.0*N* solutions in ethyl alcohol.

Qualitatively all these data are in agreement with anticipations based upon the concept of holes. It is the shape and volume of the diffusing molecule rather than its mass which determines the diffusion velocity in a given medium. Comparison of bromoform and stearic acid illustrates this. Comparison of chloroform with glycerine shows how greatly this latter is retarded by reason of its hydrogen bond forming capacity.

The influence of the medium on the rate of

TABLE II. *Diffusion coefficients and molecular weights.*

SUBSTANCE	MOLECULAR WEIGHT	$D_{20°}$(CM²/DAY)
Pyridine	79	0.89
Glycerine	92	0.35
Chloroform	119	1.08
Chloral	147	0.53
Camphor	152	0.58
Iodobenzene	204	0.81
Brom-naphthalene	207	0.60
Bromoform	252	0.83
Stearic acid	284	0.34

[10] Northrop and Anson, J. Gen. Physiol. **12**, 543 (1928).
[11] Cole and Gordon, J. Phys. Chem. **40**, 733 (1936).
[12] Anson and Northrop, J. Gen. Physiol. **20**, 575 (1937).
[13] E. Riecke, Zeits. f. physik. Chemie **6**, 564 (1890).

TABLE III. *Diffusion coefficients of bromoform in various media.*

SOLVENT	NORMALITY	α	$D_{20°}$	ΔE_{vap}
Ether	0.5	0.017	2.93	6.26
Acetone	0.5	0.018	2.32	7.27
Methyl alcohol	0.5	0.022	1.67	8.44
Benzol	1.0	0.024	1.46	7.45
Ethyl alcohol	1.0	0.028	0.835	9.97
Propyl alcohol	1.0	0.030	0.665	9.99
Amyl alcohol	1.0	0.034	0.446	10.6
50% EtOH : 50% H_2O	0.25	0.038	0.267	~10.0

diffusion of a given substance can be illustrated by Öholm's[14] data for the diffusion of bromoform in various media at 20°C.

Table III again illustrates the inverse trend of α with D and indicates the decreasing value of the diffusion coefficient with increasing energy of vaporization of the medium and increasing association of the liquid.

The data of Miller[15] on the diffusion of 0.1N iodine solutions in various organic solvents illustrate the same inverse variation of α with D as shown in Table IV. Measurements of the viscosity of the solvent were simultaneously obtained in order to test the validity of the Stokes-Einstein Eq. (4) according to which the product $D\eta$ should be constant at constant temperature. The fourth column in Table IV shows that this is only approximately true, the value $D\eta$ varying between 850 and 1544. While this variation is small compared to the variation in D(0.1576 to 2.697), it is nevertheless indicative that the Stokes-Einstein relationship is not applicable. A twofold variation in r, the radius of the diffusing molecule, would be deduced from the data. The Eyring expression (3)

$$D\eta = kT\lambda_1/\lambda_2\lambda_3$$

is, in reality, only applicable to the case of self-diffusion and viscous flow. In this equation the term λ^2, in the expression for each, cancels in the product, λ being the distance between successive potential energy minima in the particular type of motion involved. In the case of diffusion of a solute through a solvent it is not necessarily true that the λ for the solute molecule in a solution is the same as the λ for the process of viscous flow. This would be true if λ was the distance between single molecules in the liquid. For a given solute in various solvents, it is

[14] Öholm, Medd. Vet. Akad. Nobel Inst. **2**, 16 (1912).
[15] C. C. Miller, Proc. Roy. Soc. **A106**, 724 (1924).

TABLE IV. *Diffusion-viscosity data for 0.1N solutions of iodine in various solvents.*

SOLVENT	$D_{(19.90)}$	α	$D\eta_{(19.90)}$	MOLE VOL.	ΔE_{vap} KCAL./MOL.
Tetrabromethane	0.1576	0.041	1544	117	11.2
Dibromethane	0.719	0.020	1232	87	8.25
Phenetole	0.843	0.023	1111	126	—
Anisole	0.977	0.024	1056	109	8.8
Iso-amyl acetate	1.071	0.021	933	149	9.0
Brombenzene	1.038	0.017	1176	105	8.8
Carbon tetrachloride	1.177	0.019	1128	97	8.0
m-Xylene	1.454	0.017	935	123	8.8
Methyl alcohol	1.572	0.018	960	40	8.44
Benzene	1.670	0.018	1072	89	7.45
Toluene	1.686	0.016	981	106	7.99
Chloroform	1.831	0.013	1062	81	7.08
Ethyl acetate	1.859	0.014	850	98	7.78
Heptane	2.386	0.016	1148	140	7.59
Carbon disulphide	2.697	0.012	1014	60	6.6

evident, however, that, even granting the invariance of λ, the presence of λ_1, λ_2 and λ_3, the dimensions characteristic of the solvent, in the equation, means that the diffusion-viscosity product shall not necessarily be constant but vary from solvent to solvent within a certain restricted range. Miller has already pointed out that, when the data for solvents of similar chemical nature are compared, the product $D\eta$ increases as the molecular volume increases. Dibromethane and tetrabromethane, chloroform and carbon tetrachloride, ethyl acetate and iso-amyl acetate of the preceding Table IV may thus be compared. Anomalous in this respect are the data for benzene, toluene and *m*-xylene which do not show the progressive variation with volume or with heat of vaporization that might be expected. The experimental data in such a series should be restudied using the more recent techniques. Similar studies with suitably chosen solvents would serve more precisely to define the influence of the λ factors on the viscosity-diffusion product. From such data, over a range of temperatures, we can expect a material increase in our knowledge of the structural characteristics of liquids.

The data on the activation energy of viscous flow in tetrachlorethane and on the activation energy of diffusion of tetrabromethane in tetrachlorethane, already discussed, indicate that the differences in activation there found will also enter into the magnitude of the diffusion-viscosity product. Since this factor enters as an exponential, $e^{-\Delta E/RT}$, it may be of controlling importance in determining the magnitude of the variations in the value of the product for various solutions of a given solute, and, specifically, in the data for iodine just presented.

The Free Energy and Entropy of Nitrosyl Chloride

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Using the harmonic oscillator rigid rotator approximation to the partition function of nitrosyl chloride, the values of the free energy function, $(F^0-E_0^0)/T$, and the entropy, S^0, have been calculated for the ideal gas from 298.1°K to 1000°K at fifty degree intervals. By comparison with the equilibrium data for the dissociation of nitrosyl chloride, ΔE_0^0 is found to be 15,510±53 cal. It is found necessary to assume an electronic weight of four for the ground state. Although the calculated equilibrium constants agree fairly well with experiment, a definite trend in the deviations cannot be satisfactorily explained.

IN the course of the determination of the entropy of N_2O_4 from the third law value of the entropy of the $NO_2-N_2O_4$ equilibrium mixture, Giauque and Kemp[1] found it necessary to calculate the product of the moments of inertia of the NO_2 molecule in an indirect manner. Using the approximate moments of inertia obtained from electron diffraction measurements, they calculated statistically the free energy of NO_2 referred to the lowest vibrational level at 0°K. By combination of this result with the similar quantities for nitric oxide of Johnston and Chapman and those for oxygen of Johnston and Walker, and the equilibrium data of Bodenstein and co-workers for the dissociation of nitrogen dioxide into nitric oxide and oxygen, Giauque and Kemp were able to verify quite definitely a previously assigned *a priori* weight of two for the ground state of the nitrogen dioxide molecule. They were then able to calculate accurately a value of the product of the moments of inertia which gave a constant ΔE_0^0 over a wide temperature range. Since the resulting product of the moments of inertia is close to the approximate value obtained from electron diffraction measurement, this work constitutes a check on the accuracy of the equilibrium data of Bodenstein and co-workers.

In the case of nitrosyl chloride the results of electron diffraction measurements are more readily capable of interpretation than those for nitrogen dioxide.[2] It appeared to the writer, therefore, that with the accurate knowledge of the dimensions of nitrosyl chloride and the assignment of the fundamental vibration frequencies of Bailey and Cassie,[3] it should be possible to check directly the experimental measurements[4, 5] of the nitrosyl chloride dissociation equilibrium. The free energy of an asymmetrical top molecule referred to the lowest vibrational level at 0°K, with the ideal gas at a pressure of one atmosphere as the standard state is:[1]

$$(F^0-E_0^0)/T=-3/2R\ln M-4R\ln T$$
$$-R/2\ln I_1I_2I_3-R\ln p_e+R\ln\sigma$$
$$-257.401+R\sum_{i=1}^{i=3}\ln[1-\exp(-hc\nu_i/kT)], \quad (1)$$

where I_1, I_2, I_3 are the principal moments of inertia, p_e is the multiplicity of the ground state, and σ is the symmetry number, which is equal to unity for nitrosyl chloride. Unlike nitrogen dioxide, nitrosyl chloride is not an "odd" molecule; hence in the absence of contradictory evidence p_e is taken equal to unity.

Ketelaar and Palmer[2] give the following results for the dimensions of nitrosyl chloride: Cl−O = 2.65 ± 0.01A, Cl − N = 1.95 ± 0.01A, N − O = 1.14 ± 0.02A, and the O − N − Cl angle = 116±2°. If one takes the plane of the molecule as the $x-y$ plane, and the x axis through the center of gravity parallel to the O−Cl distance, the resulting moments of inertia are: $I_x=1.04\times10^{-39}$ g cm², $I_y=14.5\times10^{-39}$ g cm², $I_z=15.5$

[1] Giauque and Kemp, J. Chem. Phys. **6**, 40 (1938).
[2] Ketelaar and Palmer, J. Am. Chem. Soc. **59**, 2629 (1937).
[3] Bailey and Cassie, Proc. Roy. Soc. (London), **A145**, 336 (1934).
[4] Trautz and Wachenheim, Zeits. f. anorg. allgem. Chemie **97**, 241 (1916).
[5] Dixon, Zeits. f. physik. Chemie, Bodenstein Festband, 679 (1931).

TABLE I. *Free energy of nitrosyl chloride assuming electronic weight of unity.*

T°K	$-((F^0-E_0^0)/T)_{NOCl}$
450	56.472 cal./mole—°K
500	57.422
550	58.298
600	59.113
650	59.876
700	60.594
750	61.260

$\times 10^{-39}$ g cm^2, $I_xI_yI_z = 2.34\times10^{-115}$ g^3 cm^6. A transformation to principal axes introduces only a small change; $I_1I_2I_3 = 2.06\times10^{-115}$ g^3 cm^6. The frequency assignment of Bailey and Cassie[3] is: $\nu_1 = 1832$ cm^{-1}, $\nu_2 = 633$ cm^{-1}, $\nu_3 = 923$ cm^{-1}. The molecular weight is taken as 65.465. The errors to be expected from nonconsideration of the several isotopic species of nitrosyl chloride are negligible.[6] Following general usage, the values of the fundamental constants used are those listed in *International Critical Tables*.

Upon introduction of known quantities Eq. (1) becomes

$$-(F^0-E_0^0)/T = 4R\ln T - R\sum_{i=1}^{i=3}\ln\left[1-\exp\left(-hc\nu_i/kT\right)\right]+7.521. \quad (2)$$

The resulting values for the free energy are listed in Table I.

COMPARISON WITH EXPERIMENT

With the aid of the accurate free energy functions for nitric oxide of Johnston and Chapman,[7,8] and for chlorine of Giauque and Overstreet,[9] and the data of Table I, it is possible to calculate the quantity $\Delta(F^0-E_0^0)/T$ for the equilibrium:

$$2NOCl \rightleftharpoons 2NO+Cl_2.$$

Values of this quantity appear in Table II. Then:

$$\Delta E_0^0/T = -R\ln K_p - \Delta(F^0-E_0^0)/T. \quad (3)$$

The equilibrium has been investigated by Trautz and Wachenheim[4] and more recently by J. K. Dixon.[5] In both cases the measurements of the extent of reaction were based upon pressure changes alone. The two sets of data are in good agreement. Using Dixon's equation,[10] which reproduces his equilibrium constants well over a range of almost three hundred degrees, the writer has calculated $\Delta F^0/T = -R\ln K_p$ at fifty degree intervals over the range of the experimental measurements. Then $\Delta E_0^0/T$ was calculated by Eq. (3). The units are cal./°K or calories as the case may be.

The values of ΔE_0^0 in column 5 of Table II show a very marked rise with temperature. If a temperature independent quantity δ is chosen such that when values of $\Delta E_0^0/T$ at 450°K and 750°K are diminished by δ the resulting values for ΔE_0^0 are equal, then δ is found to be 5.673. If each $\Delta E_0^0/T$ value is decreased by 5.673, the average ΔE_0^0 resulting is 15,412±52 cal.

The fact that the quantity 5.673 is independent of temperature leads one to believe that the source of discrepancy is not the equilibrium data. One is therefore led to a consideration of the temperature independent terms of the free energy Eq. (1). The electron diffraction measurements are reliable insofar as the distances are

TABLE II. *Calculation of ΔE_0^0 for reaction* $2NOCl = 2NO + Cl_2$ *from data of Dixon.*

T°K	$\Delta F^0/T = -R\ln K_p$	$-\Delta(F^0-E_0^0)/T$	$\Delta E_0^0/T$	ΔE_0^0
450	12.023	28.103	40.126	18,050
500	7.959	28.499	36.458	18,230
550	4.677	28.945	33.622	18,500
600	1.985	29.272	31.257	18,750
650	−0.250	29.558	29.308	19,040
700	−2.121	29.799	27.678	19,360
750	−3.700	30.045	26.345	19,750

[6] Stevenson and Beach, J. Chem. Phys. **6**, 25 (1938).

[7] Johnston and Chapman, J. Am. Chem. Soc. **55**, 153 (1933).

[8] The correction applied by Witmer, J. Am. Chem. Soc. **56**, 2229 (1934) to the nitric oxide free energy function of Johnston and Chapman was not used. Johnston and Chapman used a slightly high value for the nitric oxide doublet separation, but the magnitude of the correction is negligible for the present purpose.

[9] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

[10] It might be noted in passing that an error appears on page 686 of the paper by Dixon; ΔF^0_{298} should equal 9850 rather than 8600 cal. Then ΔS^0_{298} is equal to 29.4 instead of 33.6 cal./degree.

These quantities are for the equilibrium:

$$2NOCl = 2NO+Cl_2$$

treated according to the Lewis and Randall convention. This change will alter some of the calculated results of Leermakers and Ramsperger in their work on the nitrosyl chloride, methyl alcohol, hydrogen chloride, methyl nitrite equilibrium. J. Am. Chem. Soc. **54**, 1837 (1932).

concerned. Ketelaar and Palmer[2] state, however, that because of the very nearly equal scattering powers of the nitrogen and oxygen atoms they were unable to distinguish between the structures N−O−Cl and O−N−Cl, though the latter structure was felt to be in better accord with chemical evidence. Since this question was not definitely settled, the moments of inertia were also calculated for the N−O−Cl structure. It was found, however, that the results did not differ appreciably from those obtained for the O−N−Cl configuration.

The possibility remains that the electronic weight p_e was incorrectly assumed equal to unity. Actually if a weight of four is assumed, the values of $\Delta E_0^0/T$ are diminished by the quantity $2R$ ln 4 or 5.509. This compares favorably with the value 5.673 found empirically. If the values of $\Delta E_0^0/T$ are recalculated using $p_e=4$, the results in Table III are obtained.

The deviations from the average value of ΔE_0^0 are seen to be systematic. It may be noted that a systematic trend might be expected to result from the neglecting of gas imperfection and the anharmonicity of the oscillations. The frequencies are possibly not quite correct since Bailey and Cassie,[3] using moderate resolving power found it difficult to locate exactly the band heads. Errors of this sort are not expected to be serious since the vibrational contribution to the free energy is quite small. The same is true of vibration-rotation interaction. The multiplicity of the ground level of the nitrosyl chloride seems therefore to be fixed quite definitely as four. It would be valuable if this quantity could be obtained by an independent method, such as for example the measurement of the magnetic susceptibility of the vapor.[1]

Using the average value of ΔE_0^0 given above,

TABLE III. ΔE_0^0 *for reaction* $2NOCl=2NO+Cl_2$ *assuming* $p_e=4$.

T°K	$\Delta E_0^0/T$	ΔE_0^0
450	34.617 cal./°K	15,572 cal.
500	30.949	15,475
550	28.113	15,462
600	25.748	15,449
650	23.799	15,469
700	22.169	15,518
750	20.836	15,627
	$(\Delta E_0^0)_{Av}=15,510\pm53$ cal.	

TABLE IV. *Equilibrium constants for reaction* $2NOCl=2NO+Cl_2$.

T°K	K(ATMOS.)	K (DIXON)(ATMOS.)
450	2.540×10^{-3}	2.36×10^{-3}
500	1.757×10^{-2}	1.82×10^{-2}
550	9.093×10^{-2}	9.5×10^{-2}
600	3.506×10^{-1}	3.68×10^{-1}
650	1.099	1.13
700	2.926	2.91
750	6.964	6.44

some equilibrium constants have been calculated. These and the corresponding values from Dixon's equation are given in Table IV. Except for the extreme temperatures the agreement is good. The systematic trend observed earlier in the ΔE_0^0 values of course occurs here also. Apart from the character of this trend, the deviations are within experimental error[5] (±5 percent) with the exception of the value at 750°K.

FREE ENERGY AND ENTROPY

With introduction of $p_e=4$, the free energy Eq. (3) becomes

$$-(F^0-E_0^0)/T=4R\ln T$$

$$-R\sum_{i=1}^{i=3}\ln\left[1-\exp\left(-hc\nu_i/kT\right)\right]+10.275. \quad (4)$$

The entropy expression arising upon differentiating with respect to the temperature is:

$$S^0=4R\ln T+R\sum_{i=1}^{i=3}\left(\frac{hc\nu_i/kT}{\exp\left(hc\nu_i/kT\right)-1}\right.$$

$$\left.-\ln\left[1-\exp\left(-hc\nu_i/kT\right)\right]\right)+10.275+4R. \quad (5)$$

In Table V appear values for the free energy and entropy of nitrosyl chloride calculated by means of Eqs. (4) and (5), respectively. One may now calculate the changes in the standard thermodynamic quantities at 298.1°K for the reaction $2NOCl=2NO+Cl_2$.

The value of $(F^0-E_0^0)/T$ for nitric oxide at 298.1°K is −42.985, and that for $S^0_{298.1}$ is 50.35.[7] Those for chlorine are, respectively, −45.951 and 53.31,[9] the units being cal./mole−°K. Using the value of $-(F^0-E_0^0)/T$ from Table V one

finds for the reaction $2NOCl=2NO+Cl_2$

$$\Delta(F^0-E_0^0)/T=-20.569.$$

Since $\Delta E_0^0=15{,}510\pm53$ cal.,

$$\Delta F^0_{298.1}=(298.1)(-20.569)+15{,}510=9378\pm60 \text{ cal.},$$

$$\Delta S^0_{298.1}=2(50.35)+53.31-2(64.04)=25.93 \text{ cal./°K.},$$

$$\Delta H^0_{298.1}=9378+(298.1)(25.93)=17{,}108 \text{ cal.}$$

These and the values derived from Dixon's equation are recorded in Table VI. The use of this equation for calculations at 298.1°K amounts simply to an extrapolation of over a hundred degrees below the lowest experimental temperature; and such discrepancies as are found are to be expected.

Finally the standard free energy, entropy and heat of formation of nitrosyl chloride may be found.

$\frac{1}{2}N_2+\frac{1}{2}O_2\rightarrow NO$	$\Delta F^0_{298.1}=20{,}650$ cal.,[11]
$NO+\frac{1}{2}Cl_2\rightarrow NOCl$	$\Delta F^0_{298.1}=-4{,}690$,
$\frac{1}{2}N_2+\frac{1}{2}O_2+\frac{1}{2}Cl_2\rightarrow NOCl$	$\Delta F^0_{298.1}=15{,}960$ cal.

The entropies of N_2[11], Cl_2[9] and O_2[12] at 298.1°K

TABLE V. *Free energy and entropy of nitrosyl chloride.*

T°K	$-(F^0-E_0^0)/T$ CAL./MOLE −°K	S^0 CAL./MOLE −°K
298.1	55.676	64.04
300	55.730	64.10
350	57.033	65.58
400	58.187	66.92
450	59.226	68.15
500	60.176	69.28
550	61.052	70.34
600	61.867	71.32
650	62.630	72.24
700	63.348	73.12
750	64.014	73.93
800	64.671	74.72
850	65.284	75.46
900	65.870	76.17
950	66.430	76.85
1000	66.967	77.50

[11] Giauque and Clayton, J. Am. Chem. Soc. **55**, 4875 (1933).
[12] Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).

TABLE VI. *Data for reaction* $2NOCl=2NO+Cl_2$ *and for formation of nitrosyl chloride* $2NOCl=2NO+Cl_2$.

	THIS RESEARCH	BY EQUATION OF DIXON
$\Delta F^0_{298.1}$	9378 cal.	9850 cal.
$\Delta S^0_{298.1}$	25.93 cal./deg.	29.4 cal./deg.
$\Delta H^0_{298.1}$	17,108 cal.	18,600 cal.

$\frac{1}{2}N_2+\frac{1}{2}O_2+\frac{1}{2}Cl_2\rightarrow NOCl$

$\Delta F^0_{298.1}=15{,}960$ cal.
$\Delta S^0_{298.1}=-10.03$ cal./deg.
$\Delta H^0_{298.1}=12{,}970$ cal.

are, respectively: 45.79, 53.31, 49.03 cal./deg. per mole. From Table V $S^0_{298.1}$ for nitrosyl chloride is 64.04 cal./deg. per mole.

Then

$$\Delta S^0_{298.1}=64.04-\tfrac{1}{2}(45.79+49.03+53.31)=-10.03 \text{ cal./deg.},$$

$$\Delta H^0_{298.1}=\Delta F^0_{298.1}+(298.1)\Delta S^0_{298.1}=15{,}960+(298.1)(-10.03)=12{,}990 \text{ cal.}$$

THE ELECTRONIC WEIGHT

If the electron structure of nitrosyl chloride is written down, it is seen that two electron pairs must be shared by the nitrogen and oxygen atoms. This case is analogous to that of the oxygen molecule. Reasoning further by analogy it would seem likely that the ground state of the nitrosyl chloride molecule would be triple, corresponding to parallel orientation of the spins of two electrons, and that there would be a singlet state not far above the ground level. If the energy separation of the states, Δ, is small compared to kT, the electronic partition function becomes effectively equal to four with a small temperature dependence. Thus

$$Z_{\text{elec}}=3+\exp(-\Delta/kT)\cong 4-\Delta/kT+\cdots.$$

Unfortunately the experimental data are not sufficiently accurate to permit of the determination of this energy separation. It may be said, however, that the data are so much better in accord with a weight of four than with a weight of three that the latter possibility seems definitely excluded.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Intermetallic Compounds Produced by Next Nearest Neighbor Interaction in Alloys

A glance through the phase diagrams of binary alloys shows that the formation of intermetallic compounds is an exceedingly common occurrence. Although a general interpretation may be difficult, it is of some interest to show that a simple extension of the Bragg-Williams theory of order-disorder in alloys can give certain types of such compounds in spite of the neglect of such important factors as fluctuations, lattice vibrations, lattice distortions, etc.

A convenient way of describing the long range order in a crystal is by means of the concentration of atoms of types A and B on interpenetrating sublattices, as has been done by Shockley[1] for the system copper-gold. The face-centered lattice of this system may be broken up into four sublattices having the property that any atom of one lattice has four nearest neighbors on each of the other three sublattices. If N_{A1} and N_{B1} represent the number of atoms of types A and B on lattice one, and the variable $y_1=(N_{A1}-N_{B1})/(N_{A1}+N_{B1})$ be taken as a measure of the concentration on sublattice 1, Shockley shows that the energy due to the interaction of nearest neighbors may be written, to a first approximation,

$$c(y_1y_2+y_1y_3+y_1y_4+y_2y_3+y_2y_4+y_3y_4),$$

c being a constant. The interaction of next nearest neighbors may be taken into account by further breaking up these four sublattices into a larger number and expressing their interactions as above, but using a new constant for the terms representing the more distant interactions.

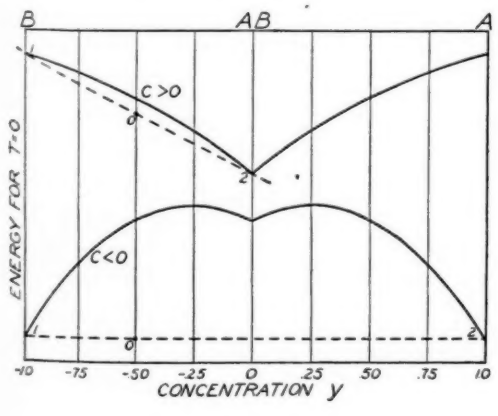

FIG. 1.

The procedure may be illustrated in the simpler case of a body-centered cubic lattice. This may be broken up into two simple cubic lattices which have the property that every atom of one lattice has its eight nearest neighbors on the other lattice. Each of these simple cubic lattices may be further broken up into two lattices which have the property that every atom of one has its six next nearest neighbors on the other. The total energy of interaction may then be written in the form

$$E=N[c(y_1+y_2)(y_3+y_4)+c'(y_1y_2+y_3y_4)],$$

c representing nearest neighbor, and c' next nearest neighbor interaction. Atoms on sublattices 1 or 2 are nearest neighbors of atoms on sublattices 3 and 4. Atoms on sublattices 1 and 3 are next nearest neighbors of atoms on sublattices 2 and 4, respectively. The entropy may be written in the form

$$\Phi=\frac{Nk}{8}\left[8\ln 2-\sum_{n=1}^{4}\{(1+y_n)\ln(1+y_n)+(1-y_n)\ln(1-y_n)\}\right].$$

Introducing the long range order variables

$$S_{12}=(y_1-y_2)/2,$$
$$S_{34}=(y_3-y_4)/2,$$
$$S=(y_1+y_2-y_3-y_4)/4$$

and the total mean concentration

$$y=(y_1+y_1+y_3+y_4)/4,$$

the energy may be written

$$E=N[2(2c+c')y^2-2(2c-c')s^2-c'(s_{12}^2+s_{34}^2)]. \quad (1)$$

The variables have the following limits

$$0\leqq|y|\leqq 1$$
$$0\leqq|s|\leqq 1-|y|$$
$$0\leqq|s_{34}|\leqq 1-|y-s|$$
$$0\leqq|s_{12}|\leqq 1-|y+s|.$$

With these equations the entire behavior of the system may be worked out. We shall here show only that the intermetallic compound AB may be formed at the absolute zero. To do this we shall find the values of the order parameters which make the energy a minimum for an alloy of arbitrary composition, and for the special case

$c'<0$ and $2c-c'>0$. This is obviously $S_{12}=S_{34}=0$ and $|S|=1-|y|$ and the equilibrium energy at absolute zero has the form

$$E=N[4(2c-c')|y|+4c'y^2],$$

which is plotted in Fig. 1. A well-known property of these curves is that if a common tangent can be drawn to two points on the curve, and the tangent is everywhere below the curve, then an alloy having a composition represented by a point between the points of tangency, as for instance point 0 on the figure, will break up into two phases having the compositions 1 and 2. For $c>0$, therefore, we shall have either pure A or pure B in equilibrium with a perfectly ordered compound AB at the absolute zero. For $c<0$ any alloy will break up into pure A and pure B, but as the temperature is raised it may happen that the intermetallic compound AB will be formed. The precise manner in which the compound and the degree of order will be influenced by the temperature will depend on the relative magnitude of the constants c and c'.

Even after including the next nearest neighbor interaction, the phase diagrams will be symmetrical in A and B, as was pointed out to me by Dr. Shockley. A term in the energy involving y to the first power has consequently been omitted as its inclusion would have no bearing on the results here discussed.

In face-centered cubic alloys compounds of the form A_3B, AB, AB_3 may be described by a similar analysis.

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April 18, 1938.

[1] W. Shockley, J. Chem. Phys. **6**, 130 (1938).

Raman Effect in Liquid Acetylene

Faint rotation lines accompanying strong Raman frequencies have been reported in α-pinene[1] and in liquid acetylene.[2] Because only the P branches of the "rotation bands" were observed there has been continued conjecture as to the origin of these lines. In connection with this problem we have reinvestigated the Raman spectrum of liquid acetylene. And in exposures up to 16 hours with slit widths varying from 0.075 to 0.23 mm no rotation lines were found. These negative results along with the alternative explanation of the α-pinene band proposed in subsequent studies on α- and β-pinene[3] militate greatly against the reality of such single-branched rotational effects.

One new line found by us corresponds to a shift of 1259 cm^{-1}. This is extremely diffuse in character and probably is an overtone of the deformation frequency at 630 cm^{-1}. Bhagavantam and Rao[4] reported a shift of 1233 cm^{-1} excited by Hg 4358A which was not excited by Hg 4047A; perhaps this is the corresponding shift in gaseous acetylene. Our shift was excited by both of the strong mercury lines.

Accompanying the strong 1961 cm^{-1} shift is a faint companion, 1934 cm^{-1}. These lines can be attributed to identical vibrations in the normal acetylene molecules and in the isotopic molecule $HC^{13}\equiv C^{12}H$. By application of the secular equation for acetylene given by Glockler and Wall[5] with force constants adjusted to fit our data the position of this isotope lines was calculated to be 1929 cm^{-1}, which is only 5 wave numbers from the observed value. This same calculation indicates that the 3341 cm^{-1} frequency also should be accompanied by an isotope line, 3330 cm^{-1}. No line was observed here.

The 1961 cm^{-1} vibration as excited by Hg lines 4339, 4348, and 4358A ["the triplet"] along with the isotope line excited by 4358A show on the photographic plate in a somewhat regular order. And these lines all fit in the "rotation series" previously reported.[2] It must be noted, however, that two additional lines not found here were reported in that series.

In gaseous acetylene Bhagavantam and Rao measured a doublet 589 cm^{-1} and 643 cm^{-1} which they attributed to the O, P, R, and S branches (Q branch missing) of the Raman active degenerate deformation frequency. According to them, their interpretation checks with data on infra-red absorption in the gas. In the liquid, however, we do not obtain results strictly analogous. We have found lines at 560 cm^{-1} and 631 cm^{-1}; the former is very weak as might be expected in view of the low temperature of observation (−75°C), but the greater doublet separation at this temperature would not be predicted. Moreover, another complication lies in the fact that the 631 cm^{-1} shift seems to consist of two distinct components when photographed under high dispersion. These are separated by 10–11 cm^{-1} with a mean value of 631 cm^{-1}. Such a splitting could not be predicted from the curves given by Bhagavantam and Rao on the construction of the doublet. These differences seem to be due to the different environment in the gaseous and liquid states.

The acetylene was prepared from pure calcium carbide, was purified by passing through a sodium plumbite-, chromic acid-, sodium hydroxide-, dehydrite-train; and by distillation.

The experimental data in summary lists the following Raman shifts: 560, 631 (625, 636), 1259, 1934, 1961, and 3341 cm^{-1}.

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May 2, 1938.

[1] B. G. Bonino and P. Cella, Mem. Acad. Italia Chim. **2**, 5 (1931).
[2] G. Glockler and C. E. Morrell, J. Chem. Phys. **4**, 15 (1936).
[3] S. K. K. Jatkar and R. Padmanabhan, Ind. J. Phys. **10**, 55 (1936).
[4] S. Bhagavantam and A. V. Rao, Proc. Ind. Acad. Sci. **3A**, 135 (1936).
[5] G. Glockler and F. T. Wall, J. Chem. Phys. **5**, 813 (1937).
* M. M. Renfrew, DuPont Fellow, 1937–8.

Errata: Thermodynamic Functions of the Chloro- and Bromomethanes, Formaldehyde and Phosgene

(J. Chem. Phys. **6**, 25 (1938))

Several errors appearing in our paper[1] were corrected in a previous note.[2] Another error has been brought to our attention. All corrections are made here, rendering our previous note superfluous.

TABLE X. ΔF^0 *of ideal gases.*

T	H_2CO	Cl_2CO	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
298.1	−27.3	−49.7	−14.2	−15.1	−15.5	−15.5
350	−27.1	−49.1	−13.3	−14.1	−14.2	−13.8
400	−26.8	−48.4	−12.3	−12.4	−12.9	−12.1
500	−26.2	−47.2	−10.1	−10.6	−10.2	−8.9
600	−25.5	−45.9	−7.9	−8.3	−7.5	−5.5
700	−24.7	−44.7	−5.5	−5.9	−4.8	
800	−24.0	−43.4	−3.2	−3.5	−1.8	
900	−23.2	−42.0	−0.7			
1000	−22.4		+1.7			
1100	−21.5		+4.2			
1200	−20.7		+6.5			
1300	−19.9					
1400	−19.1					
1500	−18.2					

The values of $-(F^0-E_0^0)/T$ in Tables VI and VIII are high by 1.987 cal./deg./mole.

The value of ΔE_0^0 for the reaction

$$C_{\beta g}+H_2+\tfrac{1}{2}O_2=H_2CO$$

from Newton and Dodge's value of K_1, is −28.30 kcal./mole. The value of ΔE_0^0 from their value of $K_2(2.09\times10^{+3})$ is −27.48 kcal./mole. The unweighted average of these two values and the thermal value gives the final value for ΔE_0^0 of −27.8 kcal./mole, instead of 27.2 kcal./mole.

The corrected free energies of formation of the gases, in kcal./mole, are given in Table X.

The free energies of formation of the liquid chloromethanes CH_2Cl_2, $CHCl_3$ and CCl_4 are, respectively, −15.5, −16.3 and −16.6 kcal./mole at 298°K.

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May 16, 1938.

[1] "Thermodynamic Functions of the Chloro- and Bromomethanes, Formaldehyde and Phosgene," J. Chem. Phys. **6**, 25 (1938).
[2] Errata, J. Chem. Phys. **6**, 108 (1938).